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Adsorption and Nitrogen Isotope Exchange on Metallic Osmium Catalysts

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Osmium catalysts prepared by decomposition-reduction of ammonium osmium chloride with hydrogen at 573°K show activated adsorption of hydrogen from 80 to 537°K. At the lowest temperature the adsorption is in part van der Waals adsorption. Van der Waals adsorption of nitrogen on the same catalyst decreases continuously from 80°K. The nitrogen isobar at 1 atmos. pressure shows a minimum at 350°K and then shows increasing adsorption to a maximum at 428°K. The increase is attributed to activated adsorption of nitrogen which velocity measurements confirm. From a nitrogen adsorption isotherm at 80°K the area per gram of catalyst is computed to be 30.8 square meters. Only 4 percent of this area is covered at 1 atmos. pressure by nitrogen at 428°K. The nitrogen adsorption is less than 10 percent of the hydrogen adsorption at 1 atmos. pressure in the temperature range of 273–573°K. Such osmium catalysts show progressive sintering when heated at 673°K. The nitrogen isotope exchange reaction $N^{28}_2+N^{30}_2=2N^{29}_2$ on these catalysts is just measurable at 473°K and very rapid at 573°K, with an activation energy of 21.8 kcal. The reaction is not second-order and is measurably inhibited by even 3 percent of hydrogen in the gas. With hydrogen concentrations of 50 percent and upwards there is no measurable exchange at 550°K. Oxygen poisons the exchange reaction which has an activation energy of 26 kcal. on the poisoned catalyst. Ammonia decomposes on the catalyst at 573°K at least 6 times as fast as the exchange reaction occurs, yielding an $N_2:3H_2$ mixture. The data on exchange point to a mechanism in which the slow process is the migration of atomically bound nitrogen on a surface on which active centers are few. Repeated adsorption and desorption of nitrogen from configurationally more complex active centers is a possible alternative mechanism for the exchange. Experiment cannot yet decide whether the breaking of bonds in the adsorption of the nitrogen molecule is the rate-determining process.

PROMOTED iron catalysts for ammonia synthesis have been the object of considerable experimental investigation relative to their adsorptive properties and the mechanism of the synthesis. Recently a study of the exchange reactions of nitrogen isotopes on such catalysts has been made by Joris and Taylor[1] which confirmed a conclusion reached from other investigations that it is the activation of the nitrogen-nitrogen bond which is the important rate-determining step in the synthesis. The study revealed that nitrogen exchange was slower than synthesis of ammonia. In his classical researches on the synthesis process, Haber[2] obtained excellent results with osmium as the catalyst. To extend the scope of our knowledge in this general field we have therefore made parallel studies on the adsorption characteristics of osmium catalysts for nitrogen and hydrogen adsorption, on the decomposition of ammonia and the nitrogen isotope exchange reaction on such surfaces, in which a single atom species is present without promoter molecules as a complicating factor.

[1] G. Joris and H. S. Taylor, J. Chem. Phys. **7**, 893 (1939).
[2] F. Haber and R. LeRossignol, Zeits. f. Elektrochemie **19**, 53 (1913).

ADSORPTION STUDIES

Gutbier and Schieferdecker[3] studied hydrogen adsorption on osmium from sodium hexachlorosmate and found a linear decrease with tem-

[3] A. Gutbier and W. Schieferdecker, Zeits. f. anorg. Chemie **184**, 305 (1929).

TABLE I. *Helium dead space measurements on catalyst No. 2 at 1 atmos. pressure.*

T°K	273	302.6	388.1	493.1	575
V_{obs}	41.3	38.5	31.5	26.3	23.3
V_{ds}	41.6	38.2	31.3	26.2	23.4$_5$

TABLE II. *Hydrogen adsorption on catalyst No. 2 at 1 atmos. pressure.*

T°K = 83	194.5	273	385	428	459	491	573
V_{H_2} =135.3	73.6	58.0	44.1	40.3	37.9	35.2	30.1
V_{ads} = 22.0	18.1	16.5	12.6	11.4	10.3	8.8	6.9

TABLE III. *Hydrogen adsorption isotherm on catalyst No. 2 at 80°K.*

P_{mm} = <1 mm	13	65	160	340	586	693	790	870
V_{ads} = 8.6	13.0	14.1	15.6	17.5	20.5	21.2	22.3	22.8

perature from 0–200° with sintering occurring at the upper temperature. Belkevich,[4] with osmium black from reduction of the chloride by hydrazine hydrochloride in alkaline solution, found that desorption at 150° was inadequate to remove adsorbed hydrogen which was released, however, at 250°. Frankenburger[5] mentions that osmium was found by Frankenburger and Hodler to show traces of nitrogen adsorption increasing with increasing temperature and irreversible. No data were given. Arnold and Burk[6] studied the decomposition of ammonia on a commercial osmium metal in the temperature range from 290–370° and concluded that the reaction was of zero order with respect to ammonia, that ammonia was more strongly adsorbed than nitrogen or hydrogen, and that hydrogen had more than twice the inhibiting effect of nitrogen. The observed activation energy for the decomposition was 42 kcal.

Experimental method and techniques

Our adsorption measurements were made in an apparatus with automatic pressure control developed by Taylor and Strother.[7] The adsorbent was disposed on Pyrex glass wool in a chamber 25 mm diameter connected by 2 mm capillary tubing to the vacuum system and gas burette fitted with supply trains. During desorption, heat was supplied by an electric furnace. Vapor baths at suitable temperatures, ice, solid carbon dioxide and liquid-air baths were used for temperature control in the adsorption measurements.

Dead-space determinations were made with helium purified by slow passage through well-evacuated charcoal cooled to liquid-air temperatures, then over reduced copper at 500° and through a solid carbon dioxide-acetone trap at −78°. Electrolytic hydrogen was passed over platinized asbestos at 250° and dried at −78°. Nitrogen was passed over heated copper at 500° and similarly dried.

Metallic osmium was prepared by the decomposition-reduction of ammonium osmium chloride in a stream of hydrogen at 300°. Contrary to data in Mellor[8] stating that a temperature of

TABLE IV. *Nitrogen adsorption on catalyst No. 2 at 1 atmos. pressure.*

T°K = 83	194.5	273	385	428	459	491	528	573
V_{N_2} =156.0	60.7	43.4	32.0	30.0	28.4	26.8	25.2	23.9
V_{ads} = 42.7	5.2	1.8	0.5	1.0	0.8	0.5	0.3	0.4

TABLE V. *Nitrogen adsorption isotherm on catalyst No. 2 at 194.5 and 273°K.*

P_{mm}	<1	6	18	44	191	357	594	747
$V_{ads(194.5°)}$	1.2	2.4	2.8	3.1	3.9	4.3	4.9	5.1
P_{mm}	8	38	138	254	368	516	646	747
$V_{ads(273°)}$	0.1	0.5	0.9	1.1	1.2	1.4	1.4	1.6

TABLE VI. *Nitrogen adsorption isotherm on catalyst No. 2 at 83°K.*

P_{mm}	<0.2	<0.2	0.2	0.5	2.0	3.0	7	15	
V_{ads}	2.1	4.0	8.6	9.7	12.0	13.1	16.3	18.6	
P_{mm}	27	48	104	178	292	371	488	598	756
V_{ads}	20.5	22.2	24.3	26.4	30.2	32.1	35.1	38.3	42.5
P_{mm}	774	817	846	874					
V_{ads}	43.3	44.9	45.5	47.9					

TABLE VII. *Isotherm of activated adsorption of nitrogen at 491°K.*

P_{mm} =2	46	104	321	456	594	697	751	
V_{ads} =0.0	0.05	0.1	0.3	0.3	0.4	0.4	0.43	

[4] P. I. Belkevich, J. Gen. Chem. USSR **9**, 944 (1939).
[5] W. Frankenburger, Zeits. f. Elektrochemie **39**, 277 (1933).
[6] E. A. Arnold and R. E. Burk, J. Am. Chem. Soc. **54**, 23 (1932).
[7] C. O. Strother and H. S. Taylor, J. Am. Chem. Soc. **56**, 586 (1934).
[8] J. W. Mellor, *Treatise on Inorganic and Theoretical Chemistry* (Longmans Green, London, 1936), Vol. 15, p. 689.

600–700° is necessary for complete reduction, titration of chloride ion in the effluent indicated substantial elimination of the chloride at 300°. The osmium could be recovered from used catalysts by distilling the volatile tetroxide from nitric acid solution into 10-percent potassium hydroxide and precipitating potassium osmate with an equal volume of ethyl alcohol.

Experimental results

Exploratory measurements on catalyst No. 1 reduced at 400° showed that desorption at this temperature sintered the catalyst continuously. Desorption at 300° removes adsorbed nitrogen to the same extent as a 400° desorption. With hydrogen the desorption at 300° was not so complete as at 400°. Lower desorption temperatures gave incomplete removal of adsorbed gas. Definite evidence of activated adsorption of nitrogen between 155 and 300° was obtained with a maximum around 184°. The adsorption of hydrogen was much greater than that of nitrogen and decreased continuously with temperature throughout the range −190 to 300°.

Definitive adsorption measurements were made on catalyst No. 2 from 8.04 g of the chloride reduced at 300° for 36 hours to yield 3.5 g osmium. A standard evacuation technique lasting 4 hours for hydrogen and 3 hours for nitrogen at 300° was adopted after controlled tests at several temperatures below this upper limiting temperature. The dead space determinations with helium in cc at NTP for a working pressure of 1 atmos. and various temperatures are given in Table I together with values calculated from the equation $V_{ds}=7.10+9408/T$, obtained by

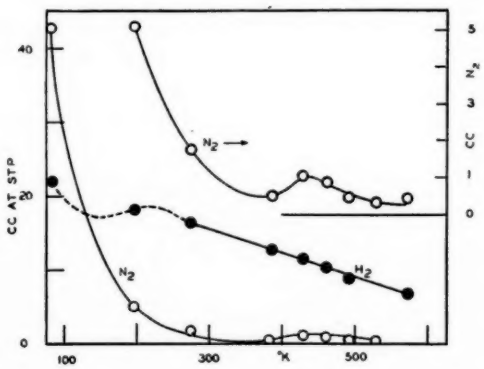

FIG. 1. Isobars at $P=1$ atmos. of hydrogen and nitrogen on osmium catalyst No. 2.

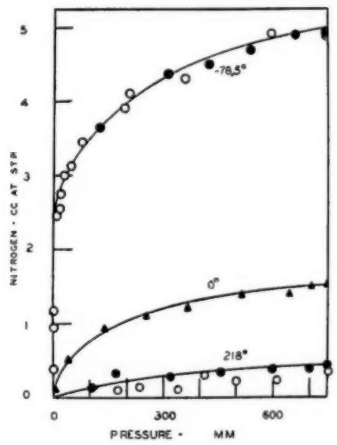

FIG. 2. Adsorption isotherms of nitrogen on osmium catalyst No. 2.

the method of least squares with the data from 273°K upwards, neglecting higher powers of T.

Hydrogen adsorption

Table II presents, V_{H_2}, the hydrogen introduced at 1 atmos. pressure to the catalyst system at various temperatures from 194.5 to 573°K and, V_{ads}, the adsorptions calculated therefrom by means of the dead space equation.

Table III presents data on the adsorption of hydrogen at 83°K at various partial pressures after the standard evacuation technique.

Nitrogen adsorption

Measurements with nitrogen are summarized in Tables IV to VII. In Table IV are given the volumes in cc of nitrogen, V_{N_2}, introduced at atmospheric pressure and at temperatures from 83 to 574°K, after standard evacuation, together with the volume adsorbed, V_{ads}, calculated therefrom with the aid of the dead space equation.

Table V gives isotherms of nitrogen adsorption at 194.5 and 273°K over a range of pressures from 0–760 mm.

In Table VI the corresponding data for an isotherm at 83°K are given in greater detail since, on the data in question, estimates are based on the available surface of the catalyst.

In Table VII are presented data on the adsorption isotherm of nitrogen at 491°K in the region of activated adsorption where the rate process was rapid enough for attainment of equilibrium.

The isobars, at $P=1$ atmos. for hydrogen and nitrogen are plotted in Fig. 1. In the inset to

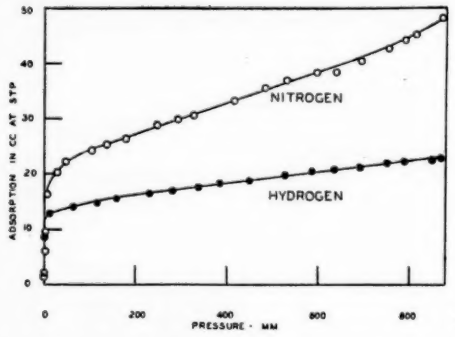

FIG. 3. Adsorption isotherms of hydrogen and nitrogen at 83°K on osmium catalyst No. 2.

the diagram the nitrogen isobar at and above 194.5°K is plotted on a volume scale multiplied by a factor of 5, the better to display the maximum around 430°K at which temperature activated adsorption alone is responsible for the observed adsorption. The adsorption isotherms at −78.5, 0° and 218°C are shown in Fig. 2. It is to be noted that the data at the two lowest temperatures do not lend themselves to calculations of the heat of adsorption because of disparity in adsorptions and the two higher temperature isotherms cannot be combined as they involve two different types of adsorption. The isotherms for nitrogen and hydrogen at 83°K are plotted in Fig. 3. The nitrogen isotherm, following the method of treatment of Emmett and Brunauer,[9] gives a "B" value of 24 cc adsorbed gas on 3.5 g osmium, equivalent to 30.8 sq. m of surface per gram of metal. The area effective in activated adsorption at atmospheric pressure is only 4 percent of this value (~1 cc) when at its maximum (428°K).

Velocity of nitrogen adsorption

Rates of adsorption for nitrogen at $P=1$ atmos. on osmium (catalyst No. 2) are presented in Fig. 4. The amount of gas introduced to keep the pressure at 1 atmos. is plotted as ordinate against time in hours as abscissae. In Figs. 2 and 4 duplicate data are plotted as circles and black dots. It will be noted that there is a measurable rate of adsorption with time at 155° but that this has become so rapid at 218 and 300° that saturation values are quickly reached.

[9] P. H. Emmett and S. Brunauer, J. Am. Chem. Soc. **58**, 1754 (1935); *ibid.* **59**, 155, 2682 (1936).

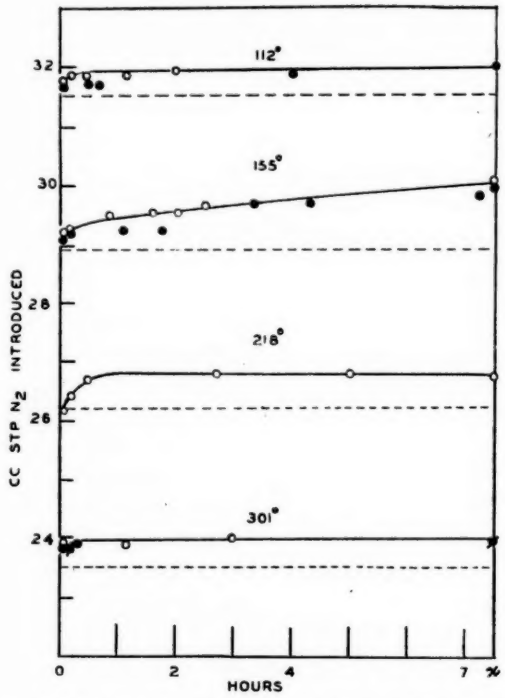

FIG. 4. Velocity of nitrogen adsorption on osmium catalyst No. 2 at 112, 155, 218 and 301°C, and 1 atmos. pressure.

At 112° the rate of adsorption is very slow after the first amount rapidly adsorbed. On the diagram the dashed lines indicate the volumes necessary to fill the dead space at each temperature.

The Nitrogen Isotope Exchange Reaction

Apparatus and materials

The measurements for the exchange reaction $N^{28}{}_2+N^{30}{}_2=2N^{29}{}_2$ were carried out in an apparatus similar to that of Joris and Taylor.[1] The osmium catalyst was contained in a quartz reaction vessel, 15 cm long and 2.2 cm internal diameter, horizontally disposed. An electric furnace 26 cm long was used to heat the catalyst chamber, the temperature being measured with a Chromel-Alumel couple located in the furnace at the central portion of the catalyst chamber. The catalyst section was shown to have a fairly uniform temperature.

The sample of nitrogen, kindly furnished by Professor H. C. Urey of Columbia University, contained about 10 percent of N^{15}, with a content of 1000 parts $N^{28}{}_2$, 103 parts $N^{29}{}_2$ and 59

parts N^{30}_2 as measured in a Bleakney crossed-field mass spectrograph. The ratio, R, for $N^{29}_2 : N^{30}_2$ was therefore 1.75. If statistical equilibrium between the three isotopic forms were to obtain (assuming $K=4$) the quantities would change to $N^{28}_2=1000$; $N^{29}_2=200$ and $N^{30}_2=10.5$ and R would have the value ~ 19.

In the present experiments analyses were made of the ratio of the mass peaks, 29 and 30, in a mass spectrograph built in this laboratory to the specifications of Nier.[10] With this instrument we have reproduced the findings of Nier as to its capacity and have tested the spectrograph in the resolution of mass peaks of water vapor, methane, neon, nitrogen, methylamine and methyl chloride, and their isotopic constituent ions. The initial value for R, the ratio of the mass peaks $N^{29}_2 : N^{30}_2$ was 1.91 in this instrument. We shall present our results on the progress of the exchange reaction in terms of a "delta value," that is the number of new molecules of N^{29}_2 formed from 100 molecules of N^{30}_2 and an equivalent number of N^{28}_2. The correlation between the ratio, R, and the delta value, d, is given by the expression

$$R=(100R_0+2x)/(100-x),$$

where $x=d/2$ and R_0 is the initial ratio. For values of R less than 5, the relationship is nearly linear or $d \approx cR$. A ratio of 5 corresponds to 55 percent of the total reaction for our initial mixture.

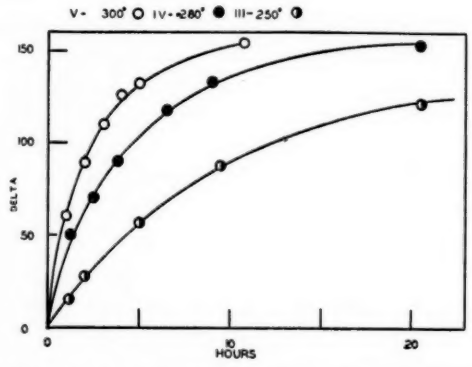

FIG. 5. Velocity of exchange of nitrogen isotopes on osmium No. 3 at 250°, ◑, 280°, ●, and 300°C, ○.

[10] A. O. Nier, Rev. Sci. Inst. **11**, 212 (1940). We wish to record our indebtedness to Professor Nier who kindly furnished us the data for construction of the apparatus prior to publication.

The nitrogen used was purified from oxygen by slow passage, immediately before use, over reduced copper heated to 500°C. In one experiment a trace of methylamine known to be present as an impurity was removed by passage of the gas through a U-tube cooled in liquid air.

Hydrogen for reduction of the catalyst *in situ* and for regenerating the catalyst poisoned by oxygen was purified as in the adsorption studies. Ammonia, free from hydrogen sulfide, was obtained by redistillation of a Barrett product.

The osmium catalyst, No. 3, used for the exchange studies was prepared by reduction-decomposition for 16 hours at 300°C of 5.68 g of the ammonium osmium chloride to yield 2.47 g of metal. Between determinations of the exchange the catalyst was evacuated for at least three hours at 300°C.

Experimental results

In the graphs of data the times of reaction are given in hours and the pressures in cm of

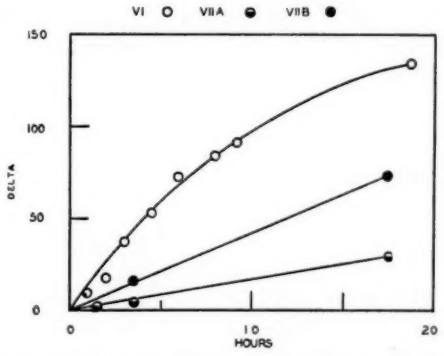

FIG. 6. Velocity of nitrogen exchange at 273°C, ○, on osmium No. 3, and at 280°, ◒ and 300°C, ● on osmium No. 3, poisoned by oxygen.

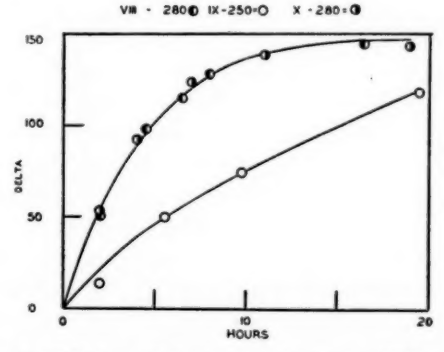

FIG. 7. Velocity of nitrogen exchange at 250°, ○, and 280°C, ◐ and ◑ on osmium No. 3 to show reproducibility of rate.

mercury. The temperatures are those recorded throughout the reaction period except in cases where large fluctuations occurred, in which cases weighted means are given.

Preliminary exploration at 9 cm initial pressure showed no exchange during 18 hours at 100°C, during a further 44 hours at 200°C the ratio R only reached 2.83 but in an additional 2.25 hours at 300° the ratio changed to 9.7, and in 5.75 hours to 14.7.

(*i*) *Activation energy of the exchange reaction.*—Figure 5 records experiments at mean temperatures of 250, 280 and 300°C. The maximum temperature variation at the two lower temperatures was ±5°C over the whole time intervals, but at 300°C the variation was markedly less. On withdrawal of samples for analysis the working pressure fell regularly from an initial value of 9–10 cm to ~4 cm after 5 or 6 withdrawals.

The activation energy calculated from the data at 250 and 280°C is 21.0 kcal.; from those at 280 and 300° the value is 21.8 kcal.

In Fig. 6 are shown data for a normal rate of exchange at 273°C and two experiments at 278 and 300° on the same catalyst after inadvertent poisoning by slight admission of air, oxygen, it is assumed, being the poison since subsequent reduction restored the activity. The data on the poisoned catalyst yield an activation energy for exchange of 26.1 kcal. After this group of measurements reduction in hydrogen for 14 hours at 300° served to eliminate a small amount of white solid (OsO_4?) and to restore activity. Figure 7 shows measurements successively at 280, 250 and 280°. It shows the reproducibility of the measurements and yields an activation energy of 21.8 kcal. in good agreement with the earlier data.

(*ii*) *Order of reaction.*—Preliminary experiments at 27 and 8 cm indicated the absence of any marked effect of pressure on the rate of reaction. Definitive experiments to test this effect as well as an inhibiting effect of hydrogen on the velocity of exchange are presented, from series XV of our measurements, in Fig. 8, in which the following sequence of measurements was made at 280°C, (A) at 8 cm initial pressure, (B) at 15.8 cm pressure, (C) at 8 cm pressure, (D) at 8 cm pressure with special technique to remove traces of methylamine from the gas,

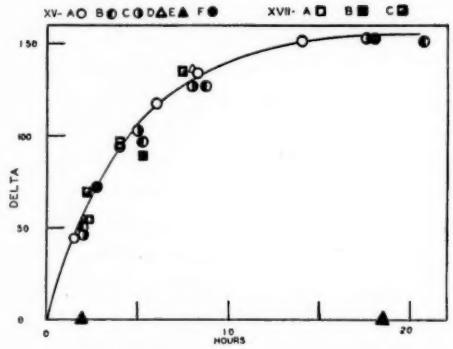

FIG. 8. Velocity of nitrogen exchange at 280°C on osmium No. 3, (A) at 8 cm pressure, ○; (B) at 15.8 cm pressure, ◐; (C) repeating (A), ◑; (D) at 8 cm removing methylamine △; (E) with a $3H_2 : 1N_2$ mixture, ▲; (F) repeating (A), ●. Series XVII (A) at 6 cm pressure, □; (B) at 6 cm pressure of N_2 containing 3.3 percent H_2, ■; (C) repeating (A), ◪.

(E) with a $3H_2 : 1N_2$ mixture at an initial pressure of 35 cm (which would have been 45 cm had the adsorption of hydrogen been the same as that of nitrogen), (F) at 8 cm pressure to check (A), (C) and the constancy of activity. The absence of any pressure influence on reaction velocity is manifest, indicating that the reaction is not second-order. Traces of methylamine appear to exert a slight inhibitory action presumably due to decomposition yielding hydrogen. A $3H_2 : 1N_2$ mixture shows no measurable exchange at 280° during 18 hours.

(*iii*) *Exchange reaction in presence of hydrogen.*—The influence of hydrogen concentration on the exchange reaction was explored in series XVI of our measurements. Using a 1 : 1 N_2-H_2 mixture no exchange occurred in 20 hours at 280°. Series XVII, also included graphically in Fig. 8, (A) with 6 cm of nitrogen, (B) with 6 cm nitrogen containing 3.3 percent hydrogen and (C) with 6 cm of pure nitrogen serves to show that even the small quantity of hydrogen in (B) had a definite inhibitory effect on the exchange. Between (A) and (B) the activity of the catalyst for ammonia decomposition was established (see below). The data of XVII (C) indicate that this may have had a slight positive influence on the catalyst activity, thus emphasizing the inhibitory action of hydrogen in XVII (B).

(*iv*) *Ammonia decomposition on catalyst No. 3.*—The exchange apparatus was not well adapted to measurement of rate of ammonia decomposition and the adsorptive capacity of the catalyst

for ammonia, hydrogen and nitrogen further complicated the measurement of rate. In three experiments interpolated between the exchange experiments, series XVII (A) and (B), decomposition of the ammonia at 300°C was established. On the catalyst, after standard evacuation, the introduction of ammonia in an amount which would have developed 10 cm pressure had it been nitrogen, gave an initial pressure of 3.7 cm which increased to 4.7 cm in one hour. After a ten-minute evacuation a similar charge of ammonia developed an initial pressure of 5.5 cm which increased to 7.1 cm in 96 minutes. At this point it was shown, by withdrawal of the gas and immediate reintroduction, that diffusion of undecomposed ammonia through gaseous products to the surface was a rate-determining factor since, in the minute of time consumed in the withdrawal and reintroduction, the pressure increased to 7.7 cm. After 12 hours the final pressure was 11.8 cm and the gas was analyzed as $3H_2 : 1N_2$ with less than 5 percent undecomposed ammonia. A third experiment with an initial pressure of 36.3 cm gave an off-gas after 9 hours with a composition 16 percent NH_3; 16 percent N_2; 68 percent H_2. This catalyst was evidently much more active than those used by Arnold and Burk.*

General Discussion

The speed of the reaction which is measured cannot be faster than the rate of desorption of nitrogen. This becomes equal to the velocity of adsorption at temperatures where equilibrium isobars are established for the process of activated adsorption. Such temperatures are often much higher than the temperatures at which activated adsorption becomes measurable. Our measurements are in agreement with these observations. Activated adsorption is rapid at 150°C; the speed of the process which we measure is not comparably rapid until a temperature at least 100° higher is attained.

Ammonia decomposition to yield nitrogen-hydrogen gas also involves nitrogen desorption. Our experiments indicate that the ammonia decomposition reaction at 300° is faster than the exchange reaction with pure nitrogen and, from our experiments on the retarding influence of hydrogen on the exchange reaction, would be very much faster than this latter in a $N_2 : 3H_2$ mixture. The isotope exchange reaction appears therefore to be slower than the rate of nitrogen desorption. This result parallels the earlier result with decomposition and exchange on iron.[1]

There are several possibilities for the explanation of such a result. With molecules adsorbed atomically on widely separated active centers the exchange process may require migration of atoms to new positions favorable to exchange, and this migration may be rate determining. Our adsorption studies indicate sparse coverage of the surface by activated adsorption of nitrogen which, at the maximum, reaches only 4 percent of the surface accessible to nitrogen for van der Waals adsorption. At 250°C and 1 atmos. pressure only 2 percent of the surface is so covered. The temporary poisoning of the catalyst by oxygen, in amounts so small that a material loss of vacuum, due to nitrogen simultaneously entering, was never noticed, also corroborates the evidence that sites are few.

For the more rapid ammonia decomposition, migration of nitrogen atoms, if rate determining, can only involve much shorter distances of migration. Our results on ammonia decomposition point to a stronger adsorption of ammonia than of nitrogen at the decomposition temperatures, in agreement with the findings of Arnold and Burk. A greater area of the surface adsorbing ammonia as compared with nitrogen implies both an increased number of nitrogen atoms having adjacent neighbors and shorter distances of migration if necessary. Reaction between impinging molecules of ammonia and adsorbed nitrogen atoms would also contribute to a faster ammonia decomposition. This possibility could not be important however if the process, as Arnold and Burk concluded, were of zero order on the catalyst.

The parallelism between the results on iron promoted catalysts and osmium does not extend to the influence of hydrogen on the exchange process. In the former case, hydrogen accelerates exchange. With osmium, even 3 percent of hydrogen in the nitrogen is definitely inhibitory and large amounts suppress the exchange. The strong adsorption of hydrogen on osmium, more

* Data supplied by Dr. Arnold confirm this conclusion.

than 15 times that of nitrogen in the temperature range of the exchange process, means that, in a nitrogen-hydrogen mixture, the probability of nitrogen-hydrogen atom neighbors is much greater than that of nitrogen-nitrogen atom neighbors. The adsorbed hydrogen will also impede a migration process over the surface. In the case of iron at the temperature of exchange ($\sim$500°C), there is no such preferential hydrogen adsorption. Indeed, it has been shown by Brunauer and Emmett that chemisorption of nitrogen on doubly promoted catalysts markedly decreases their high-temperature, type B, chemisorption of hydrogen.[11]

We may now mention two other possibilities that may govern the rate of nitrogen exchange. In the first place, if migration was not involved, the exchange must take place on configurationally more complex sites capable of accommodating at least two molecules of nitrogen adsorbed adjacently. In such case, exchange could occur by adsorption-desorption without migration. Owing, however, to the composition of the gas mixture (86 percent $N^{28}{}_2$: 8.8 percent $N^{29}{}_2$: 5.2 percent $N^{30}{}_2$) the probability of adsorptions favorable to exchange $0.86\times0.052=0.045$ is small compared to that of adsorptions which will not produce exchange, $(0.86)^2+(0.86\times0.09)+(0.09\times0.05)=0.80$.* Evidently the fruitful adsorptions would only be 5 percent of the total adsorptions of nitrogen molecule pairs. This restriction does not occur in the case of ammonia decomposition so that it would be possible thus to account for a 20-fold difference in velocity between exchange and ammonia decomposition in this manner. The retarding influence of hydrogen on the exchange is so great, however, that the difference in velocity, at equal hydrogen concentrations on the surface, is very much greater than the 20-fold difference possible with a mechanism of adsorption-desorption on 2-molecule sites. With sites adsorbing more than two molecules adjacently, the fruitful adsorptions would be a larger fraction of the total, in which case ammonia decomposition and nitrogen exchange would be more nearly equal in velocity, again contrary to experiment.

In the earlier paper on the exchange on iron catalysts Joris and Taylor[1] pointed out that the activated adsorption of nitrogen might involve only a portion of the valence bonds without complete dissociation of the molecule to atoms. On this basis, the slow process might involve the rupturing of the residual valencies. The data of Brunauer and Emmett[11] appear to compel the conclusion that, in the case of iron, the activated adsorption involves interaction of surface atoms with atomic nitrogen. In the present case no such evidence is yet available and so the mechanism must remain as one to be included in any comprehensive consideration of the problem.

Our data on the activation energies of exchange on osmium and iron, $E=22$ and ~50 kcal., respectively, suggest a greater lability of nitrogen on the osmium surface and a weaker Os$-$N bond than the Fe$-$N bond. This is in agreement with expectation in view of the known nitrides of iron and the absence of such compounds of osmium. Activated adsorption and desorption of nitrogen on osmium occurs in a lower range of temperature than it occurs on iron which fact also points to a weaker Os$-$N linkage.

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[11] S. Brunauer and P. H. Emmett, J. Am. Chem. Soc. **62**, 1732 (1940).

* It is to be noted that any combination of $N^{28}{}_2$ or $N^{29}{}_2$ molecules on a 2-molecule adsorption site cannot result in exchange, neither can a combination of $N^{30}{}_2$ and $N^{29}{}_2$; hence the form of the expression used.

Vibrations of Long Chain Molecules; Raman Spectra of *n*-Octane, Decane, Cetane and Eicosane in the Liquid State

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The Raman spectra of *n*-octane, decane, cetane and eicosane in the liquid state have been photographed. With increasing chain length the low-lying Raman lines ($<800\ cm^{-1}$) become few in number and very diffuse. This observation is interpreted in terms of a number of chain configurations co-existing in the liquid state in contrast to the extended configuration found by x-ray analysis of crystalline paraffins. Theoretical investigations which assume that the carbon atoms in a chain are coplanar are not applicable to data obtained for liquid (and gaseous) paraffins.

WITHIN the last few years a considerable interest has grown in the structure and vibrations of long chain molecules such as those of the higher normal paraffins. Many papers have dealt with both the theoretical and the experimental aspects of this problem. While real progress has been made a number of important questions still await an answer.

The present situation with regard to the molecular structure of these compounds appears to be as follows: For crystalline paraffins the x-ray analysis of Muller[1] leads him to conclude that the molecules lie parallel in their extended configuration in which all of the carbon atoms are in the same plane. This is consistent with the results of x-ray analysis of other organic crystals containing paraffinic chains. For gaseous paraffins there is no such direct information. However, entropy considerations,[2] an analysis of vapor viscosity data,[3] and a statistical calculation of chain lengths[4] agree in predicting an average configuration of the chain which is quite far from the extended one.

There is even greater uncertainty in the case of liquids. The small difference in density between liquid and solid paraffins suggests that no great change occurs on melting and that the chain molecules even in the liquid might be mainly in their extended, planar configuration. On the other hand, there is the possibility that this configuration is greatly dependent on the ordered arrangement of the molecules in the crystal lattice, and that when the ordered arrangement is destroyed on fusion the molecules become distributed among the various configurations permitted by their geometry and packing.

To learn more about the vibrations of long chain molecules in the liquid state the Raman spectra of four representative paraffins have been studied. Data for two of these, *n*-octane and *n*-decane, have previously been reported by other investigators and will be referred to later. The experimental conditions have been described earlier.[5]

DATA

Octane

This was supplied by Dr. G. Calingaert via Dr. A. V. Grosse and the Universal Oil Products Company. Its boiling point was 125.6° (corr.); n_D^{20} 1.3975.

280(5*b*)(*k*,*i*±*e*), 297(1*vd*)(*e*), 354(1*vd*)(*k*,*e*), 378(1*vd*)(*k*,*e*), 398(0*vd*)(*e*), 426(1*vd*)(*k*,*e*), 766(0*vd*)(*k*,*e*), 807(0*d*)(*k*,*e*), 817(1*b*)(*k*,*e*), 842(1*vd*)(*k*,*e*), 862(2)(*k*,*e*), 878(3)(*k*,*e*), 895(4)(*k*,*e*), 956(0)(*k*,*e*), 968(1*d*)(*k*,*e*), 1027(1*d*)(*k*,*e*), 1046(1)(*k*,*e*), 1062(2)(*k*,*i*,*e*), 1085(3*d*)(*k*,*i*,*e*), 1136(2*d*)(*k*,*e*), 1163(1*vd*)(*k*,*e*), 1301(5*b*)(*k*,*i*,*e*), 1345(0)(*k*,*e*), 1368(0)(*k*,*e*), 1438(7*b*)(*k*,*e*), 1459(7*b*)(*k*,*e*), 2712(1)(*k*,*e*), 2732(2)(*k*,*e*), 2851(10)(*q*,*p*,*k*,*i*,*e*), 2862(2)(*p*,*k*,*i*,*e*), 2875(3)(*p*,*k*,*i*,*e*), 2901(2*vd*)(*k*,*e*), 2917(2*vd*)(*i*?,*e*), 2939(10)(*q*,*p*,*k*,*i*,*e*), 2963(10)(*q*,*p*,*k*,*i*,*e*).

Decane

This sample was synthesized by Dr. K. N. Campbell of Notre Dame University. Its physical

[1] Muller, Proc. Roy. Soc. **A120**, 437 (1928).
[2] Huggins, J. Chem. Phys. **8**, 181 (1940).
[3] Melaven and Mack, J. Am. Chem. Soc. **54**, 888 (1932).
[4] Laskowski and Burk, J. Chem. Phys. **7**, 465 (1939).
[5] Rosenbaum, Grosse and Jacobson, J. Am. Chem. Soc. **61**, 689 (1939).

constants were: boiling point, 172.1–172.2/729 mm; n_D^{20} 1.4114.

228(1)(*k*,±*e*), 254(1*d*)(*k*,*e*), 275(1)(*k*,±*e*), 355(0)(*k*,*e*), 403(1*d*)(*k*,*e*), 773(0*vvd*)(*e*), 807(0*d*)(*e*), 844(1*d*)(*k*,*e*), 868(0*d*)(*k*,*e*), 887(0*d*)(*k*,*e*), 900(0)(*k*,*e*), 920(1*d*)(*k*,*e*), 1047(0)(*e*), 1062(2*b*)(*k*,*e*), 1077(1*d*)(*k*,*e*), 1090(1*d*)(*k*,*e*), 1134(2*b*)(*k*,*e*), 1160(0)(*k*,*e*), 1302(5*b*)(*k*,*e*), 1317(0)(*k*,*e*?), 1342(0)(*k*,*e*), 1365(0*d*)(*k*,*e*?), 1437(7*b*)(*k*,*e*), 1456(7*b*)(*k*,*e*), 2731(1)(*k*,*e*), 2852(10*b*)(*q*,*p*,*k*,*i*,*e*), 2876(6)(*p*,*k*,*i*,*e*), 2894(10*vd*)(*q*,*p*,*k*,*i*,*e*), 2939(10)(*q*,*p*,*k*,*i*,*e*), 2962(10)(*q*,*p*,*k*,*i*,*e*).

Cetane

The sample, kindly lent by Dr. H. Pines of The Universal Oil Products Company, had a boiling point of 286.5±1°, corr; n_D^{20} 1.4342.

224(1*vd*)(*e*), 281(0*d*)(*k*,*e*), 403(1*d*)(*e*), 722(0*d*)(*e*), 832(1)(*e*), 843(1)(*e*), 866(1)(*k*,*e*), 892(2*b*)(*k*,*e*), 960(1,double?)(*e*), 1020(0?)(*e*), 1063(3)(*k*,*e*), 1078(3*b*,unsym.)(*k*,*e*), 1108(0)(*e*), 1131(3)(*k*,*e*), 1163(0)(*e*), 1272(0?)(*e*), 1301(6*b*)(*k*,*e*), 1344(0*d*)(*k*,*e*), 1367(0*d*)(*k*,*e*), 1437(7*b*)(*k*,*e*), 1457(7*b*)(*k*,*e*), 2716(0*d*)(*k*,*e*), 2730(1)(*k*,*e*), 2851(10*b*)(*q*,*p*,*o*,*k*,*i*,*e*), 2890(10*b*)(*q*,*p*,*k*,*e*), 2937(10*b*)(*p*,*k*,*i*,*e*), 2962(8)(*q*,*p*,*k*,*i*,*e*).

Eicosane

Part of a sample furnished by Professor E. E. Reid to Professor W. D. Harkins was used; its melting point was 36.4–36.8°. This substance was kept in the liquid state by heat from the mercury arcs. Since it showed fluorescence when irradiated with the Hg 4047 line, only photographs taken with a $NaNO_2$ filter were evaluated.

407 (0*vd*)(*e*), 848(0*d*)(*e*), 871(0*d*)(*e*), 891(0*d*)(*e*), 1067(1)(*e*), 1088(2*vb*,double?)(*e*), 1135(1)(*e*), 1306(5*b*)(*e*), 1441(6*b*)(*e*), 1460(6*b*)(*e*), 2727(0*d*)(*e*), 2851(10*b*)(*e*), 2864(1)(*e*), 2893(10)(*e*), 2934(9*d*)(*e*), 2961(4*d*)(*e*).

Discussion

To facilitate comparison, the data for octane and decane are listed in Table I together with the values of Kohlrausch and Köppl.[6]

The vibrations of chain molecules have many times been the subject of theoretical investigation,[7–12] almost all of which has proceeded on the assumption that the chain elements are coplanar. The results obtained in such investigations have been applied to the Raman and infra-red spectra of normal paraffins in the liquid and gaseous states. As indicated above, it is by no means clear that a comparison of these theoretical frequencies with the experimental data is justified. Indeed the following considerations point in just the opposite direction.

Table I.

R.	K. and K.	R.	K. and K.
		Octane	
280(5*b*)	281(5*b*)	1062(2)	
297(1*vd*)			1074(5, *dop*)
	346(00)	1085(3*d*)	
354(1*vd*)		1136(2*d*)	1135(3)
378(1*vd*)		1163(1*vd*)	1163(0)?
398(0*vd*)		1301(5*b*)	1300(6*b*)
426(1*vd*)	420(0)	1345(0)	
766(0*vd*)		1368(0)	1372(00)
807(0*vd*)		1438(7*b*)	
817(1*b*)			1446(9*sb*)
842(1*vd*)		1459(7*b*)	
862(2)	861(3)	2712(1)	
878(3)		2732(2)	2730(2*b*)
	889(4*sb*)	2851(10)	2852(15*b*)
895(4)		2862(2)	
956(0)		2875(3)	2876(15*b*)
968(1*d*)	966(3*b*)	2901(2*vd*)	2900(12)
1027(1*d*)		2917(2*vd*)	
	1040(3*b*)	2939(10)	2933(12)
1046(1)		2963(10)	2962(10)
		Decane	
228(1)		1062(2*b*)	
	243(3*b*)	1077(1*d*)	1076(4, *dop*)
254(1*d*)		1090(1*d*)	
275(1)		1134(2*b*)	1136(3)
355(0)		1160(0)	
403(1*d*)	405(0)		1174(1)
	720(0)?	1302(5*b*)	1302(6*b*)
773(0*vd*)		1342(0)	
807(0*vd*)		1365(0*d*)	
	820(2)		1379(0)?
844(1*d*)		1437(7*b*)	1437(6*b*)
868(0*d*)		1456(7*b*)	1457(6*b*)
887(0*d*)			2722(2*b*)
	895(2*b*)	2731(1)	
900(0)		2852(10*b*)	2850(12*b*)
920(1*d*)		2876(6)	2876(12*b*)
	955(1)	2894(10*vd*)	2905(12*b*)
	1012($\frac{1}{2}$)	2939(10)	2932(10)
1047(0)		2962(10)	2960(9)

[6] Kohlrausch and Köppl, Zeits. f. physik. Chemie **B26**, 209 (1934).

[7] Bartholome and Teller, Zeits. f. physik. Chemie **B19**, 366 (1932).

[8] Bauermeister and Weizel, Physik. Zeits. **37**, 169 (1936).

[9] Mecke, Zeits. f. physik. Chemie **B36**, 347 (1937).

[10] Kirkwood, J. Chem. Phys. **7**, 506 (1939).

[11] Whitcomb, Nielsen and Thomas, J. Chem. Phys. 8, 143 (1940).

[12] Pitzer, J. Chem. Phys. **8**, 711 (1940).

Approximating the CH_2 (or CH_3) group by a single particle and assuming these to be coplanar in the chain, the number of in-plane vibrational modes is $2N-3$, where N is the number of carbon atoms. One would predict then that as the length of the chain increases, the number of Raman lines with frequency below 1000 cm^{-1} should increase rapidly. This is not in agreement with observation. One of the striking points about the spectra reported here is the fact that the number of Raman lines actually decreases in the order decane, cetane, eicosane. In addition, the few lines with frequency below 800 cm^{-1} become exceedingly broad and diffuse. It is not likely that the observed decrease in the number of lines is a simple matter of intensity because the exposure time for compounds of high molecular weight was made correspondingly long.

If three positions of equilibrium, analogous to those in ethane, exist about each carbon-to-carbon bond (excepting those configurations excluded for steric reasons) the above observations find a very natural qualitative explanation. As Bauermeister and Weizel[8] have shown, the deformation frequencies depend on the chain configuration. As the length of the chain increases, the number of possible configurations increases very rapidly. Because of the low symmetry of the molecules in any configuration except the planar one, the selection rules do not limit the number of Raman lines. Hence instead of a set of more or less sharply defined lines, the Raman spectrum of a long chain liquid paraffin would show a roughly continuous distribution, with only those low-lying lines appearing which happen to be common to a group of configurations; these lines would presumably be broad and diffuse.

The interpretation suggested here gains support from earlier results on short chain paraffins. Kohlrausch[13] has called attention to the facts that *n*-butane has a larger number of Raman lines than can be accounted for on the basis of a planar configuration and that the difference, expected from symmetry considerations, in the number of lines of even and odd membered chains does not exist. Also the number of Raman lines is greater for *n*-propyl than for isopropyl derivatives and a similar difference exists between *n*-butyl and tert-butyl derivatives. Kohlrausch has explained all these facts in terms of a number of possible configurations ("rotation isomers") and this is completely consistent with the present interpretation of the observations on long chains.

If this interpretation is valid it follows that the planar configuration is not uniquely stable but is just one of a large number of configurations of approximately equal probability. This has as an unfortunate consequence the fact that the theoretical treatment of actual chain vibrations (including the calculation of thermodynamic quantities) is very much more complicated than it would otherwise be—and even for planar chains the problems of the torsional modes and their interaction with the others has not been adequately solved. The theoretical results obtained up to the present time have value primarily as the basis for further work; any numerical computations of vibrational entropy should be regarded with reserve. In particular, numerical values obtained by assuming a certain number of 1000 cm^{-1}, 290 cm^{-1} and 120 cm^{-1} frequencies should be considered as frankly empirical.

I wish to thank those whose generosity in making pure compounds available made this investigation possible. I also wish to acknowledge the valuable assistance given by Mr. C. Roger Sandberg.

[13] Kohlrausch, *Das Smekal-Raman Effekt* (Julius Springer 1938), p. 169.

On the Anharmonicity of Vibrations of Polyatomic Molecules. I

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Several simplifying assumptions concerning the vibrational potential energy of polyatomic molecules are discussed and tested by means of the available experimental material. One of these assumptions furnishes relations between the higher coefficients of the potential energy of molecules containing several equivalent bonds. If a molecule contains p equivalent bonds XY, the potential energy of the corresponding symmetric stretching vibration, and only of this one, can be approximated by means of a Morse function with the constants pD and $a/\sqrt{p}$ in the place of D and a. The anharmonicity factors of bending vibrations are small if the third-order coefficient of the potential energy vanishes on account of the symmetry of the molecule.

THE general theory of vibrations and the approximating function of Morse together with an ample supply of experimental data have furnished an exhaustive description of the vibrations of diatomic molecules. In the much more complicated case of polyatomic molecules the data usually do not supply sufficient information for a complete description. The harmonic approximation, outlined by Dennison years ago, has been successfully applied in a number of cases. The deviations from this approximation, however, have not yet been satisfactorily represented in a general way.

Manneback[1] has first discussed anharmonicity in connection with relations which are special cases of the product rule. Tchang,[2] following a suggestion made by Lemaitre, applied the same anharmonicity correction to all carbon-hydrogen vibrations in his calculations on ethylene. De Hemptinne and Delfosse[3] tested the Birge-Sponer relation between anharmonicity and dissociation energy on the data of ammonia, phosphine and arsine. The author[4] suggested that the same anharmonicity correction, derived from infra-red data, be applied only to CH *stretching* vibrations, and inferred, on the basis of inadequate experimental material, that the anharmonicity factor of bending vibrations is small.

Considerable difficulty in disentangling infra-red spectra is caused by the fact that the data available for determining anharmonicity factors are, as a rule, insufficient. Therefore relations of a general nature will be useful in the analysis of spectra. In addition, the lack of anharmonicity corrections impairs the evaluation of bond constants. As has been previously pointed out,[5] this correction is by no means negligible.

The problem consists, of course, in finding relationships which will reduce the number of anharmonic coefficients to be determined empirically. If this problem can be solved, a more or less accurate description of anharmonicity will be achieved beyond those very few cases in which adequate data are available.

Obviously this problem can be attacked only with the aid of far-reaching simplifications. Two appropriate starting points offer themselves: assumptions which have proved useful in the first-order description of polyatomic molecules and relations applied to the anharmonicity of diatomic molecules. It is the purpose of this paper to enumerate and test these various relationships.

ASSUMPTIONS TO BE TESTED

In the following a group or bond XY in a molecule will be called "single" if the molecule does not contain another group XY situated on an equivalent place. "Equivalent" groups or bonds are the two CH of acetylene or the two OH of water.

A bending vibration will be called "even" if the two halves of the vibration are symmetric

[1] C. Manneback, Ann. Soc. Scient. Bruxelles **B55**, 237 (1935).
[2] Y. L. Tchang, Ann. Soc. Scient. Bruxelles, [I] **58**, 87 (1938).
[3] M. de Hemptinne and J. M. Delfosse, Bull. Acad. Sci. Roy. Belg. **21**, 793 (1935).
[4] O. Redlich, J. Chem. Phys. **7**, 856 (1939).
[5] For instance, by Ta-You Wu and A. T. Kiang, J. Chem. Phys. **7**, 178 (1939).

with respect to, and perpendicular to a symmetry plane of the molecule. The terms of the potential energy containing odd powers of a bending coordinate of this sort vanish on account of the symmetry.

The fundamental difference with regard to anharmonicity between stretching (valence) and bending (deformation) vibrations is obvious. Indeed, any reasonable potential energy function must involve a negative value different from zero of the coefficient correlated with the third power of *any* "single" stretching coordinate while the third-order coefficient of some bending coordinates necessarily vanishes.

The potential energy of a molecule can always be expressed in terms of stretching and bending coordinates of the individual bonds. The first assumption will be: (A) The interaction or cross terms of higher than second order containing stretching coordinates of different nonequivalent groups may be neglected. A similar assumption (B) will be tested concerning the omission of higher cross terms containing bending or bending and stretching coordinates of different nonequivalent bonds.

These assumptions are of course similar to Bjerrum's valence force system. They may perhaps be expected to cause in the anharmonic constants relative errors of the same order of magnitude as the valence force system does in the quadratic constants. However, deviations of such kind will not do much harm inasmuch as the anharmonic terms represent a correction only.

As bending vibrations are generally more susceptible to interaction, we shall expect that assumption (B) will hold to a lesser degree than assumption (A).

Further, it will be interesting to see whether the contribution to the potential energy of a "single" stretching coordinate is approximated by a Morse function[6] (assumption C). This function, of course, cannot fit a bending vibration.

The well-known relation which connects the anharmonicity factor and the dissociation energy of diatomic molecules has been accepted in the case of polyatomic molecules by Ellis[7] and by Dadieu and Kohlrausch[8] and rejected by Badger and Binder.[9] Properly restricted, it will appear to deserve a test (assumption D).

While these assumptions are expressed with respect to stretching and bending, i.e., geometrical coordinates, the experimental data refer to normal coordinates. The relationship between the two kinds of coordinates is sometimes trivial on account of the symmetry. However, if two or more vibrations possess the same symmetry properties the second-order coefficients required for the transformation can be determined only in the case of some hydrogen compounds by means of an investigation of the related deuterium compounds. Otherwise some special simplifying assumption (E) is to be introduced for the purpose of connecting the geometrical with the normal coordinates.

Vibrations of molecules composed of atoms of widely different masses can be approximated by a model in which infinite mass is attributed to the heavy atoms so that only the light atoms are oscillating. It is above all the hydrogen vibrations which are strongly affected by anharmonicity owing to the large amplitudes. Just in this case the latter assumption may be used for a first approximation where the data for a more precise calculation are lacking.

Several Equivalent Bonds

The foremost opportunity of testing the assumptions discussed above will be offered by the conclusions to be drawn with respect to molecules containing several equivalent bonds.

The anharmonic part of the potential energy of a pair of atoms XY will be represented by

$$V' = E_1 s^3 + E_2 t^3 + E_3 s^2 t + E_4 s t^2 + F_1 s^4 + F_2 t^4 + F_3 s^2 t^2 + F_4 s^3 t + F_5 s t^3, \quad (1)$$

where s and t are the stretching and one bending coordinate. The second bending coordinate will not be required in the following.

The anharmonic part of the potential energy of a molecule is obtained according to assump-

[6] A Morse function has already been used for representing the corresponding part of the potential energy of carbon dioxide by A. Adel and D. M. Dennison, Phys. Rev. **44**, 99 (1934).

[7] J. W. Ellis, Phys. Rev. **33**, 27 (1929).

[8] A. Dadieu and K. W. F. Kohlrausch, Ber. d. D. Chem. Ges. **63**, 251 (1930).

[9] R. M. Badger and J. L. Binder, Phys. Rev. **37**, 800 (1931).

tions (A) and (B) by composing terms like (1) without adding terms which contain coordinates of different bonds.

As a preparatory step for the change to normal coordinates, the coordinates s_1, t_1, s_2, $t_2\cdots$ of several equivalent groups are to be transformed into symmetry coordinates σ_1, τ_1, σ_2, $\tau_2\cdots$. The transformation to be applied depends on the symmetry group which results from the symmetry group of the molecule when we omit the symmetry elements on which the bond XY is situated. We shall call this group the "particular symmetry" of XY in the molecule (e.g., the symmetry C_3 for Cl in $CHCl_3$, the symmetry V for H in CH_4, etc.). In general, the required transformation is a special case of the transformations permissible under the particular symmetry, the choice being restricted by the symmetry elements on which the bond is situated.

In case the molecule contains two equivalent XY bonds (e.g.: H_2O, C_2H_2) the transformation is given for any of the various compatible symmetries by

$$\begin{aligned} s_1&=(1/\sqrt{2})(\sigma_1+\sigma_2)\,; \quad t_1=(1/\sqrt{2})(\tau_1+\tau_2)\,;\\ s_2&=(1/\sqrt{2})(\sigma_1-\sigma_2)\,; \quad t_2=(1/\sqrt{2})(\tau_1-\tau_2), \end{aligned} \tag{2}$$

where σ_1 is symmetric and σ_2 antisymmetric with respect to the symmetry element on which XY is not situated.

Thus we have for any twofold particular symmetry:

$$\begin{aligned} V'=&2^{-\frac{1}{2}}E_1(\sigma_1^3+3\sigma_1\sigma_2^2)+2^{-\frac{1}{2}}E_2(\tau_1^3+3\tau_1\tau_2^2)\\ &+2^{-\frac{1}{2}}E_3(\sigma_1^2\tau_1+\sigma_2^2\tau_1+2\sigma_1\sigma_2\tau_2)\\ &+2^{-\frac{1}{2}}E_4(\sigma_1\tau_1^2+\sigma_2\tau_2^2+2\sigma_2\tau_1\tau_2)\\ &+\tfrac{1}{2}F_1(\sigma_1^4+6\sigma_1^2\sigma_2^2+\sigma_2^4)\\ &+\tfrac{1}{2}F_2(t_1^4+6\tau_1^2\tau_2^2+\tau_2^4)\\ &+\tfrac{1}{2}F_3(\sigma_1^2\tau_1^2+\sigma_1^2\tau_2^2+\sigma_2^2\tau_1^2+\sigma_2^2\tau_2^2)\\ &+\tfrac{1}{2}F_4(\sigma_1^3\tau_1+3\sigma_1\sigma_2^2\tau_1+3\sigma_1^2\sigma_2\tau_2+\sigma_2^3\tau_2)\\ &+\tfrac{1}{2}F_5(\sigma_1\tau_1^3+3\sigma_1\tau_1\tau_2^2+3\sigma_2\tau_1^2\tau_2+\sigma_2\tau_2^3). \end{aligned} \tag{3}$$

Similar expressions can be derived for other particular symmetries. Some of the transformation matrices required are readily derived from matrices listed in an earlier paper.[10]

[10] O. Redlich and H. Tompa, J. Chem. Phys. 5, 529 (1937).

As a general result of transforming into symmetry coordinates the coordinates of p equivalent XY groups we may state that the potential energy always contains the terms

$$p^{-\frac{1}{2}}E_1\sigma_1^3+p^{-1}F_1(\sigma_1^4+\sigma_2^4), \tag{4}$$

where σ_1 denotes the symmetric, and σ_2 the antisymmetric coordinate (except for threefold symmetry where no antisymmetric vibration occurs). The term containing σ_2^3 vanishes. Similar results hold, of course, for the bending coordinates.

Here and later "symmetric" means "symmetric with respect to the particular symmetry."

Normal Coordinates

The experimental data usually refer to the dimensionless coordinates, introduced by Dennison,

$$x_i=2\pi(\omega_i c/h)^{\frac{1}{2}}q_i, \tag{5}$$

where ω_i denotes the frequency extrapolated to infinitesimal amplitude, and q_i the normal coordinate expressed in gram$^{\frac{1}{2}}$·cm. The potential energy, in reciprocal centimeters, is given by

$$\begin{aligned} V=&\tfrac{1}{2}\omega_1x_1^2+\tfrac{1}{2}\omega_2x_2^2+\cdots+\alpha_1x_1^3\\ &+\alpha_2x_1^2x_2+\cdots+\beta_1x_1^4+\cdots. \end{aligned} \tag{6}$$

Each x_i is in general a function of all stretching and bending coordinates

$$\begin{aligned} x_1&=\eta_{11}\sigma_1+\eta_{12}\tau_1+\eta_{13}\sigma_2+\cdots,\\ x_2&=\eta_{21}\sigma_1+\eta_{22}\tau_1+\eta_{23}\sigma_2+\cdots \end{aligned} \tag{7}$$

and so on. This may be simplified sometimes to

$$\begin{aligned} x_1&=\epsilon_1\sigma_1\,;\\ \epsilon_1&=2\pi(c/Nh)^{\frac{1}{2}}\cdot10^{-8}\omega_1^{\frac{1}{2}}f_1=0.17266\omega_1^{\frac{1}{2}}f_1 \end{aligned} \tag{8}$$

and so on because of the molecular symmetry or by a special assumption (E). The factors $f_1, f_2\cdots$ are the square roots of "reduced masses" and depend on the vibration form, the atomic masses and sometimes on molecular parameters. Avogadro's number N has been inserted so that the atomic weight scale may be used in $f_1, f_2\cdots$. Stretching and bending coordinates will be expressed in angstrom units, hence the factor 10^{-8}.

The relationship between the potential constants $\alpha_1\cdots$ and $E_1\cdots$ is obtained by a com-

parison of Eqs. (3) and (6) with the aid of either (7) or (8). In the latter, simpler case we have $E_1=2^{\frac{1}{2}}\epsilon_1^3\alpha_1$ and so on.

Stretching Vibrations and Morse's Function

In this section we shall draw a few conclusions from the more special assumption (C) according to which a Morse function

$$V=D[1-\exp(-as)]^2$$
$$=D\left[a^2s^2-a^3s^3+\frac{7}{12}a^4s^4-\cdots\right]=D\sum_{j=2}^{\infty}M_js^j \quad (9)$$

approximates those terms of the potential energy which depend only on the stretching coordinate s of a single bond.

Transforming the stretching coordinates s_ϱ of p equivalent XY groups by means of

$$s_\varrho=p^{-\frac{1}{2}}\sum_{k=1}^{p}u_{\varrho k}\sigma_k, \quad (10)$$

we have, according to assumption (A), for the stretching potential energy of the molecule

$$V=D\sum_j M_jp^{-j/2}\sum_\varrho\left(\sum_k u_{\varrho k}\sigma_k\right)^j. \quad (11)$$

For the set of transformation coefficients correlated with the symmetric coordinate σ_1, and only for this set, we have $u_{\varrho 1}=1$, so that the part of V corresponding to the symmetric stretching vibration is represented by

$$V_1=pD\sum_j M_jp^{-j/2}\sigma_1^j$$
$$=pD[1-\exp(-p^{-\frac{1}{2}}a\sigma_1)]^2. \quad (12)$$

Thus the *potential energy of a symmetrical stretching vibration*, and only of this one, *can be approximated by a Morse function*, the constants of which are correlated in a simple way with the constants of the diatomic group.

Consequently we are able to express the third- and fourth-order coefficients in terms of D and the frequency ω_1. We may consider the terms of Eq. (6) which contain only x_1 as the first terms of a Morse function (12). Identifying the coefficients we obtain

$$\alpha_1=-\left(\frac{\omega_1}{2}\right)^{\frac{3}{2}}(pD)^{-\frac{1}{2}};$$
$$\beta_1=\frac{7}{48}\cdot\frac{\omega_1^2}{pD}; \quad \text{or} \quad \beta_1=\frac{7\alpha_1^2}{6\omega_1}. \quad (13)$$

Regarding the interpretation of the quantity D, the remark following Eq. (21) applies, of course, also to Eqs. (13).

The Water Vapor Molecule

The best basis for testing the assumptions discussed above is offered by the exhaustive analysis of the vibrations of the monomeric water molecule recently carried out by Darling and Dennison.[11]

The antisymmetric bending vibration τ_2 vanishes on account of the symmetry of the molecule. The connection between the coordinates x_1, x_2 and x_3 of Darling and Dennison and σ_1, τ_1 and σ_2 is represented by the Eqs. (7). The numerical values

$$\begin{aligned}&\eta_{11}=+10.498; && \eta_{12}=+0.6387;\\ &\eta_{21}=-0.0304; && \eta_{22}=+6.7874;\\ &\eta_{33}=-11.296\end{aligned} \quad (14)$$

have been obtained from the relations

$$\sigma_1=2^{-\frac{1}{2}}q\sin\varphi+2^{\frac{1}{2}}y\cos\varphi;$$
$$\tau_1=2^{-\frac{1}{2}}q\cos\varphi-2^{\frac{1}{2}}y\sin\varphi;$$
$$\sigma_2=-2^{\frac{1}{2}}x\cdot M\sin\varphi/(M+2m\sin^2\varphi) \quad (15)$$

with the aid of the coefficients given by Darling and Dennison for the transformation of their geometrical coordinates q, y, x into the normal coordinates q_1, q_2, q_3 of Eq. (5). The angle 2φ is the angle between the two bonds, M and m are the masses of oxygen and hydrogen, respectively. The coefficients η_{13}, η_{23}, η_{31}, η_{32} are equal to zero for reasons of symmetry.

Substituting $\eta_{ij}=0.17266\omega_i^{\frac{1}{2}}f_{ij}$ we have

$$\begin{aligned}&f_{11}=+0.97906m^{\frac{1}{2}}; && f_{12}=+0.05957m^{\frac{1}{2}};\\ &f_{21}=-0.00431m^{\frac{1}{2}}; && f_{22}=+0.96272m^{\frac{1}{2}};\\ &f_{33}=-1.03869m^{\frac{1}{2}}.\end{aligned} \quad (16)$$

[11] B. T. Darling and D. M. Dennison, Phys. Rev. **57**, 128 (1940).

TABLE I. *Constants of the potential energy of water.*

TERM	COEFFICIENTS OF EQ. (6) D. AND D.	COEFFICIENTS OF EQ. (3) BY MEANS OF		
			EQ. (7), (14)	EQ. (8), (17)
x_1^3	$\alpha_1=-300$*			
x_1^3	$\alpha_1=-322$	E_1	$-5.27\cdot10^5$	$-5.64\cdot10^5$
$x_1x_3^2$	$\alpha_5=-909$		-5.74	-5.86
x_2^3	$\alpha_2=-\ 47$	E_2	-0.12	-0.23
$x_1^2x_2$	$\alpha_3=+\ 1$	E_3	-0.97	$+0.01$
$x_2x_3^2$	$\alpha_6=+160$		$+0.91$	$+2.04$
$x_1x_2^2$	$\alpha_4=+216$	E_4	$+1.43$	$+1.63$
x_1^4	$\beta_1=+\ 27.6$*			
x_1^4	$\beta_1=+\ 39$	F_1		$+10.3$
$x_1^2x_3^2$	$\beta_5=+212$			$+10.3$
x_3^4	$\beta_3=+\ 35$			$+11.4$
x_2^4	$\beta_2=+\ 2$	F_2		$+0.05$
$x_1^2x_2^2$	$\beta_4=-116$	F_3		-13.3
$x_2^2x_3^2$	$\beta_6=-108$			-13.7

* From the Morse relation (13).

If we introduce the special assumption (E) that the first and second vibration are carried out only by the hydrogen atoms we have

$$f_1=f_2=m^{\frac{1}{2}} \tag{17}$$

for the coefficients of Eq. (8) which correspond to f_{11} and f_{22} in (16) while f_{12} and f_{21} are dropped. The differences are of the order of magnitude of m/M.

Considerably better is the agreement obtained by neglecting only the term containing $\sigma_1\tau_1$ of the potential energy. In this case we have

$$\begin{aligned} f_{11}&=+0.9790m^{\frac{1}{2}}; \quad f_{12}=+0.0676m^{\frac{1}{2}}; \\ f_{21}&=-0.0013m^{\frac{1}{2}}; \quad f_{22}=+0.9671m^{\frac{1}{2}}. \end{aligned} \tag{18}$$

Comparison with (16) shows that a similar assumption may be useful where the coefficients of the exact transformation are lacking.

Table I contains the coefficients $\alpha_1\cdots\beta_6$ of Eq. (6) as given by Darling and Dennison and the coefficients $E_1\cdots F_3$ of Eq. (3). Two sets of transformation coefficients were used in correlating the coefficients of the Eqs. (3) and (6), namely (14) according to (7), and (17) according to (8).

Only the simplified transformation has been used for the fourth-order coefficients. The more precise one requires the determination of two more coefficients F_4 and F_5. The corresponding coefficients of $x_1^3x_2$, $x_1x_2^3$ and $x_1x_2x_3^2$ do not appear among the experimental data because these terms do not contribute to the vibrational energy as far as the usual approximation (second-order perturbation) is concerned. The remaining equations are not suitable for a determination of F_4 and F_5 owing to the extreme influence of small experimental errors. Therefore, only the results of the simplified transformation are given, which is consistent with the omission of F_4 and F_5.

As Eq. (3) contains less coefficients than (6), the coefficients E_1, E_3, F_1 and F_3 can be derived independently from two or three empirical constants. The various values of E_1, F_1 and F_3 agree satisfactorily with one another. There is a serious discrepancy only between the two values of E_3 derived from α_3 and α_6. The corresponding term contains the bending coordinate and, as mentioned in the introductory section, interaction between different bonds is more likely to affect bending vibrations.

Except again for E_3 the values obtained by means of the simplified transformation agree sufficiently with the results of the more precise calculation.

It is remarkable that the coefficient E_2 of the third-order pure bending term is small even in this case which deviates widely from the "even" vibration. Likewise the fourth-order bending coefficient F_2 is small in comparison with the stretching coefficient F_1, thus confirming a previous surmise that the harmonic approximation holds considerably better for bending than for stretching vibrations.

The values of α_1 and β_1 calculated according to the Morse function from Eq. (13) represent a rough approximation. The dissociation energy[12] $D=38{,}700$ cm^{-1} has been used.

CARBON DIOXIDE

On account of the symmetry, the simplified transformation is strict for carbon dioxide. The square roots of the "reduced masses" of Eq. (8) are

$$f_1=m^{\frac{1}{2}}; \quad f_2=f_3=[Mm/(M+2m)]^{\frac{1}{2}}, \tag{19}$$

where M and m denote the atomic weights of carbon and oxygen, respectively.

[12] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York), p. 53.

The vibrational analysis carried out by Adel and Dennison was recently revised by Dennison.[13] Table II contains the results.

A close inspection of the data and of Dennison's equations indicates that the discrepancies between the various values of the stretching coefficients E_1 and F_1 are hardly larger than the probable experimental error. The difference, however, between the two values of the stretching-bending coefficient F_3 cannot be explained by the uncertainty of the data. The bending coefficient F_2, somewhat uncertain as Dennison obtained two different numerical values, is small in any case.

These results are closely similar to the outcome of the preceding test of water.

The values of a and d calculated according to the Morse relation (13) with[14] $D=59{,}200$ cm^{-1} differ considerably from the experimental values. The deviations are such as would result from an excited state of the dissociation products.

Acetylene

The analysis of the vibrations of acetylene[15] has not furnished enough equations for a determination of the potential constants. The assumptions discussed in this paper yield more than the equations additionally required for a solution. A preliminary inspection, however, shows that they are inconsistent with Ta-You Wu's data. This is not surprising considering the complicated character of the relations involved and the large influence of small experimental errors.

Moreover, the assignment of the bands does not seem to be quite certain. Checking Ta-You Wu's anharmonicity factors by application of the product rule to the totally symmetric vibrations of C_2HD, we find a discrepancy of 1.1 percent which is perhaps a little more than the uncertainty of the frequencies of C_2HD. While neither of the suggested assignments is entirely satisfactory, consideration of accidental resonance between the symmetric and the antisymmetric hydrogen valence vibrations (cf. reference 11) will perhaps remove the discrepancies.

Anharmonicity and Dissociation Energy

The experimental data for the vibrational energy are usually represented, according to the result of a second-order perturbation calculation, in the form

$$W=W_0+\sum_i X_i n_i+\sum_{ij} X_{ij} n_i n_j, \qquad (20)$$

where the n_i's are the vibrational quantum numbers.

The maximum energy which can be accumulated in the ith vibration, i.e., the maximum value of W as a function of n_i ($n_j=0$ for $j\neq i$) is obtained just as in the diatomic case:

$$D_i=-X_i^2/4X_{ii}. \qquad (21)$$

The applicability of this relation depends, as it does in the diatomic case, on two conditions (assumption D).

First, whether the quantity D_i has any meaning beyond the definition given above; practically, whether the products of dissociation are in the states to which the thermochemically determined dissociation energy refers.

The available thermochemical data (cf. reference 12) for molecules with several equivalent groups are average bond energies and apply strictly, therefore, only to symmetric vibrations in which all equivalent bonds are dissolved simultaneously. But the experimental fact that the energy of the same bond is approximately the same irrespective of in which molecule the

Table II. *Constants of the potential energy of carbon dioxide.*

Term	Coeff. of Eq. (6)	Coeff. of Eq. (3)
x_1^3	$a=-51$*	
x_1^3	$a=-30$	$E_1=-7.0\cdot10^5$
$x_1x_3^2$	$c=-250$	-9.3
$x_1x_2^2$	$b=+71.3$	$E_4=+2.2$
x_1^4	$d=+2.2$*	
x_1^4	$d=+1.5$	$F_1=+12.5$
$x_1^2x_3^2$	$h=+8.9$	$+6.0$
x_3^4	$f=+6.4$	$+12.4$
x_2^4	$e=\begin{cases}+0.5\\-3.7\end{cases}$	$F_2=\begin{cases}+0.1\\-0.5\end{cases}$
$x_1^2x_2^2$	$g=+1.9$	$F_3=+2.1$
$x_2^2x_3^2$	$i=-25.7$	-14.0

* From the Morse relation (13).

[13] A. Adel and D. M. Dennison, Phys. Rev. **43**, 716 (1933); **44**, 99 (1933); D. M. Dennison, Rev. Mod. Phys. **12**, 175 (1940).

[14] Reference 12, pp. 123, 182.

[15] G. B. B. M. Sutherland, Phys. Rev. **43**, 883 (1933); G. Herzberg and J. W. T. Spinks, Zeits. f. Physik **91**, 386 (1934); Ta-You Wu and A. T. Kiang, J. Chem. Phys. **7**, 178 (1939); Ta-You Wu, *ibid.* **8**, 489 (1940).

TABLE III. *Anharmonicity factors of symmetric stretching vibrations.*

SUBSTANCE	X_i	D (REF. 12)	X_{ii}(CALC.)	X_{ii}(OBS.)	REF.
H_2O	3693.9	38700	−44.0	−43.89	11
H_2S	2610.8	30700	−28.6	−33.3	17
CO_2	1321.7	59200	− 3.7	− 0.3	13
C_2H_2(C : C)	1984	43200	−22.8	−11	15
C_2H_2(CH)	3421	30600	−47.8	−49	15
HCN(CN)	2041.0	50600	−20.6	+51.8	18
$CHCl_3$(CH)	3080.4	30600	−77.5	−60.6	19

bond occurs, indicates that the bond energies may also be used for each of several consecutive steps of dissociation.

However, antisymmetric and degenerate vibrations are excluded by the first condition at least from an immediate application of Eq. (21) because one of the dissociation products or both are in a state of strain, the accumulated potential energy being of the order of magnitude of the dissociation energy.[16]

For symmetric vibrations, still the possibility of a strain in a nondissociating bond and of excited states must be kept in mind.

The second condition of validity consists in that Eq. (20), with empirical coefficients adjusted to low quantum numbers, must sufficiently approximate the energy function in the range of high quantum numbers. A necessary, though by no means sufficient, condition of this extrapolation can be derived from a discussion of the third-order term.

If we represent the vibrational energy of one vibration by

$$W = W_0 + X_i n_i + X_{ii} n_i^2 + Y_i n_i^3, \quad (22)$$

the maximum energy

$$\Delta = D_i F(\eta); \quad F(\eta) = \frac{4}{\eta}\left[1 - \frac{2}{3\eta} + \frac{2}{3\eta}(1-\eta)^{\frac{3}{2}}\right]; \quad \eta = 3X_i Y_i / X_{ii}^2 \quad (23)$$

is obtained where D_i is defined by Eq. (21). The function $F(\eta)$ increases slowly for small values of η as indicated by the values $F(-\frac{1}{2}) = 0.94$; $F(0) = 1$; $F(+\frac{1}{2}) = 1.11$. It reaches a maximum $F(1.0718) = 1.39$ at $\eta = 8 - 4\sqrt{3}$ and decreases rapidly for higher values of η: $F(\frac{3}{2}) = 1.065$; $F(2) = 0.667$; $F(3) = 0.198$, etc.

Frequently a probable upper limit of Y_i will be derived from the experimental data. In case $\eta < 8 - 4\sqrt{3} = 1.0718$ the limit of error introduced by neglecting Y_i can be estimated with the aid of Eq. (23).

The data for the CH vibration of hydrocyanic acid give $\eta = 2.52$. For values $\eta > 1.08$ the large influence on Δ of small variations of Y_i indicates that the convergence of the series (22) is too poor for an application of Eq. (21) or even (23).

While no distinction between stretching and bending vibrations is made in the derivation of Eq. (21) the data discussed below show definitely that its validity is restricted to stretching vibrations.

Previously restricted to symmetric vibrations, Eq. (21) applies therefore to precisely the same cases which are approximated by the Morse function. As the Morse function furnishes a similar relation the validity of Eq. (21) in the case of symmetrical stretching vibrations apparently may be explained by its approximate coincidence with the Morse relation.

A symmetric stretching vibration carried out by p equivalent groups XY dissolves at the same time p bonds. Hence the maximum energy D_i of Eq. (21) is equal to pD where D denotes the dissociation energy of the bond XY. This is consistent with (4) and (13) since the square of the third-order coefficient and the first power of the fourth-order coefficient are contained in X_{11}.

The experimental material, expressed in cm^{-1}, has been collected in Table III. The values for hydrogen sulfide[17] have been derived from the Raman frequency $\nu = 2610.8$, given by Murphy and Vance, and from the first harmonic $(2\nu) = 5155$, determined in the infra-red by Bailey, Thompson and Hale.

The high positive value of X_{ii} for the CN

[16] In the case of an antisymmetric stretching vibration of p equivalent bonds the potential energy accumulated in the $p/2$ nondissociating bonds is equal to the energy required for dissolving $p/2$ bonds. It may be expected, therefore, that Eq. (21) applies to this case with $D_i = pD$ where D denotes the bond energy. Thus we obtain the following values of X_{33} (for the data cf. Table III)

	H_2O	CO_2	H_2S	C_2H_2
Calc.	−46.6	−11.8	−28.4	−44.2
Obs.	−46.37	−12.5	− 8.9	− 5

The discrepancies might well be explained by the uncertainty of the experimental data as only the figures given for H_2O and CO_2 are reliable.

[17] C. R. Bailey, J. W. Thompson and J. B. Hale, J. Chem. Phys. **4**, 625 (1936); A. H. Nielsen and H. H. Nielsen, *ibid.* **5**, 277 (1937); G. M. Murphy and J. E. Vance, *ibid.* **6**, 426 (1938).

vibration of hydrocyanic acid,[18] based upon a single band 4994 cm^{-1} of Adel and Barker, will require a special explanation. Quite apart from any special formula like Eq. (21), a high positive value of an anharmonicity factor could result only from an extremely high value of a fourth-order or interaction coefficient of the potential energy, either very improbable.

Lindholm's data for the CH vibration of the same substance are $X_3=3368.59$; $X_{33}=-55.477$; $Y_{333}=0.768$. Slight changes, permissible on account of experimental uncertainty, would bring these constants into agreement with Eq. (23). However, this agreement is insignificant for the reason discussed above.

Ellis[19] obtained nearly coincident values of the anharmonicity factors of chloroform, hexane, cyclohexane, benzene and aniline. However, the most obvious interpretation according to which all overtones belong to one vibration is certainly erroneous at least in the cases of benzene and cyclohexane. Since these substances possess a center of symmetry, odd and even harmonics of the same fundamental cannot both be found in absorption. Thus the overtones gathered in one series by Ellis originate at least in these cases from two or more fundamentals. In Table III only chloroform is included which is not subject to objections of that sort.

The agreement between the calculated and observed values of X_{ii} is satisfactory, except for HCN.

Table IV contains the anharmonicity factors of a few bending vibrations.[20] They are small in the case of "even" vibrations, and somewhat higher for water and hydrogen sulfide which deviate widely from this case. This shows that the anharmonicity factor is by far most affected by the corresponding third-order term of the potential energy.

TABLE IV. *Anharmonicity factors of bending vibrations.*

SUBSTANCE	X_{ii}	SUBSTANCE	X_{ii}
H_2O	−19.5	HCN	−2.9
H_2S	−24	N_2O	−2.2
CO_2	− 1.3	COS	−0.10
C_2H_2	−11		

CONCLUSIONS

According to assumption (A) the higher coefficients of the potential energy correlated to all stretching vibrations of several equivalent bonds are determined by one third-order and one fourth-order constant. While this result appears to be fairly well confirmed by all six available checks, the corresponding assumption (B) for terms containing bending coordinates failed in two of three cases.

The order of magnitude of all coefficients of pure stretching terms can be predicted by means of the Morse function[21] and assumption (A). The anharmonicity factors of symmetric stretching vibrations can usually be predicted by means of Eq. (21) with a fair degree of approximation.

No method has been discussed of predicting coefficients of anharmonic terms containing bending coordinates. However the anharmonicity factors of bending vibrations have been found to be small where the odd power terms of the potential energy vanish for reasons of symmetry.

While the assumptions (A) and (D) are about as well confirmed as could be expected, the methods suggested can by no means be claimed to yield more than a first approximation. Owing to their comparative simplicity they will, perhaps, be useful where preliminary or approximate information is sought, i.e., as a help in the analysis of spectra and in the calculation of force constants.

The application of these methods to cases where the experimental material is insufficient will be discussed on a later occasion.

The author is indebted to Dr. C. Zener for interesting discussions.

[18] A. Adel and E. F. Barker, Phys. Rev. **45**, 277 (1934); G. Herzberg and J. W. T. Spinks, Proc. Roy. Soc. London, **A147**, 434 (1934); E. Lindholm, Zeits. f. Physik **108**, 1455 (1938).

[19] J. W. Ellis, Phys. Rev. **33**, 27 (1929).

[20] Nitrous oxide: E. F. Barker, Phys. Rev. **38**, 1827 (1931); **41**, 369 (1932). Carbon oxysulfide: P. F. Bartunek and E. F. Barker, *ibid.* **48**, 516 (1935).

[21] It will be interesting to see whether Eq. (13) will hold better than the assumption that the constants E_l and F_l of Eqs. (1) and (3) depend only on the nature of the group XY. So far no material is available for a test.

The Cadmium Photosensitized Reactions of Propane*

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An investigation has been made of the cadmium (5^3P_1) photosensitized reactions of propane and of propane-hydrogen mixtures at a temperature of 310°C. The main products are hydrogen and hexanes, together with smaller amounts of methane, butane, pentanes and heptanes. The quantum efficiency of propane decomposition is roughly 0.6. The results indicate that the primary reaction is a C−H bond split,

$$Cd(^3P_1)+C_3H_8=CdH+C_3H_7.$$

The main secondary reactions are

$$H+C_3H_8=C_3H_7+H_2$$
$$2C_3H_7=C_6H_{14}.$$

The liquid products of the reaction appear to be mainly 2,3-di-Me-butane and/or 2-Me-pentane. This indicates that mainly secondary hydrogens are attacked, yielding the isopropyl radical. More C−C bond splitting occurs than is the case in the mercury photosensitized reaction at the same temperature. A possible explanation of this is that reactions are occurring which involve the CdH molecule.

INTRODUCTION

CONSIDERABLE information about elementary processes has been obtained from previous work on the mercury photosensitized reactions of ethane[1–4] and propane,[5] the cadmium photosensitized reactions of ethane,[6] and the reactions of atomic hydrogen with ethane,[7–9] propane[7,10,11] and butane.[7,12] The present paper is a continuation of this work, and deals with the cadmium photosensitized reactions of propane. In particular, it is of interest to compare the cadmium and mercury photosensitized reactions under similar conditions.

The reaction of hydrogen atoms, produced by the discharge tube method, with propane was investigated by Steacie and Parlee[10,11] over a range of temperatures from 25° to 250°C. They found that at low temperatures the sole product of the reaction was methane, while at higher temperatures ethane and ethylene were also formed. They concluded that the primary step was the reaction

$$H+C_3H_8=C_3H_7+H_2 \quad (1)$$

analogous to the results with ethane. At low temperatures the results could only be explained on the basis of "atomic cracking" reactions,

$$H+C_3H_7=CH_3+C_2H_5, \quad (2)$$

$$H+C_2H_5=2CH_3, \quad (3)$$

followed by

$$CH_3+H=CH_4. \quad (4)$$

At higher temperatures they postulated the additional secondary reactions

$$C_3H_7=C_2H_4+CH_3, \quad (5)$$

$$2CH_3=C_2H_6, \quad (6)$$

$$H+C_2H_4=C_2H_5, \quad (7)$$

$$H+C_2H_5=C_2H_6, \quad (8)$$

$$H_2+C_2H_5=C_2H_6+H. \quad (9)$$

The mercury photosensitized reactions of propane and of propane-hydrogen mixtures were investigated by Steacie and Dewar.[5] They found that from 24° to 323°C the products of the reaction, both with propane alone and with propane-hydrogen mixtures, were almost ex-

* Contribution No. 974 from the National Research Laboratories, Ottawa, Canada.

[1] E. W. R. Steacie and N. W. F. Phillips, J. Chem. Phys. **6**, 179 (1938).
[2] E. W. R. Steacie and N. W. F. Phillips, Can. J. Research **B16**, 303 (1938).
[3] E. W. R. Steacie, W. A. Alexander and N. W. F. Phillips, Can. J. Research **B16**, 314 (1938).
[4] E. W. R. Steacie and R. L. Cunningham, J. Chem. Phys. **8**, 800 (1940).
[5] E. W. R. Steacie and D. J. Dewar, J. Chem. Phys. **8**, 571 (1940).
[6] E. W. R. Steacie and R. Potvin, J. Chem. Phys. **7**, 782 (1939).
[7] N. R. Trenner, K. Morikawa and H. S. Taylor, J. Chem. Phys. **5**, 203 (1937).
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[9] E. W. R. Steacie and N. W. F. Phillips, J. Chem. Phys. **4**, 461 (1936).
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[11] E. W. R. Steacie and N. A. D. Parlee, Can. J. Research **B17**, 371 (1939).
[12] E. W. R. Steacie and E. A. Brown, J. Chem. Phys. **8**, 734 (1940).

clusively hydrogen, hexanes (mainly 2,3-di-Me-butane and 2-Me-pentane) and a small amount of higher hydrocarbons. There appears to be no doubt that with propane alone the primary step is

$$C_3H_8+Hg(^3P_1)=C_3H_7+H+Hg(^1S_0) \quad (10)$$

or $$=C_3H_7+HgH.$$

In the presence of hydrogen, on account of its very high quenching efficiency, almost all the excited mercury atoms will transfer their energy to hydrogen, and the primary step will be

$$H_2+Hg(^3P_1)=2H+Hg(^1S_0). \quad (11)$$

The principal secondary reactions are, apparently, in both cases

$$2C_3H_7=C_6H_{14}, \quad (12)$$

$$2H=H_2, \quad (13)$$

$$H+C_3H_8=C_3H_7+H_2. \quad (1)$$

At first sight these results appear to conflict with those of Steacie and Parlee, discussed above. The primary step in their investigation is undoubtedly reaction (1). However, their results suggest that reactions (2) and (5) are of prime importance, while the absence of methane in the mercury photosensitized reaction proves that they are unimportant even at high temperatures. However, in the case of mercury photosensitization the concentration of hydrogen atoms is very low, and that of propane relatively high, thus making reaction (2) unimportant compared with (1). Furthermore, recombination reactions of radicals will be favored by the higher pressure, thus diminishing the chance of (5). The results of the two investigations are thus not in any way incompatible.

Experimental

The lamp-reaction vessel system has been previously described.[13] The lamp consisted of a double U of Corex D tubing, the ends of which were joined to Pyrex tubes into which were sealed standard neon sign "coated" electrodes. It contained a small piece of cadmium (about 0.1 gram), and was filled with neon at 3 mm pressure. The lamp was outgassed, filled, etc., by the usual neon sign technique. It was operated at 100 milliamperes from a 6000-volt sign transformer.

[13] E. W. R. Steacie and R. Potvin, Can. J. Research **B16**, 337 (1938).

A Pyrex reaction vessel, 8 cm in diameter and 21 cm long, was sealed directly to the lamp, only the electrode chambers remaining outside. The vessel was provided with connections for the circulation of gases, and a Corex D window to permit spectroscopic observation of the radiation from the lamp. The entire lamp-reaction vessel system, including the electrodes, was placed in an electric furnace which was thermostatically controlled and was maintained at temperatures in the neighborhood of 300°C.

The total output of the lamp was estimated, by the methods previously discussed,[6] to be, very roughly, 6×10^{-6} Einstein per sec. Since it is intended to make an accurate determination of the quantum yields of this and other cadmium photosensitized reactions in the near future, only relative rates and the order of magnitude of the quantum yield will be reported here. About 60 percent of the total radiation of the lamp was the resonance line 3261A. The remainder was distributed mainly over lines at 3404, 3466, 3613, 4678, and 4800A. None of the lower resonance line 2288A was present, since the Corex D of which the lamp was constructed filtered this out completely. We are, therefore, dealing only with $Cd(5^3P_1)$ atoms, and $Cd(5^1P_1)$ atoms are not involved.*

The reaction system has already been described in detail.[1, 6, 13] A magnetically operated pump circulated the gases through the reaction vessel, and then through a cooled trap to remove products of higher molecular weight. The gases then passed through a cadmium saturator, filled with a cadmium-tin alloy, and maintained at temperatures from 250° to 300°C in various experiments. The gases then passed back to the reaction vessel. No appreciable deposition of cadmium occurred in the reaction vessel. The system was also provided with a McLeod gauge, diffusion pump, manometers, gas reservoirs, and an outlet through which samples of gas could be removed for analysis.

After the completion of an experiment the gaseous products of the reaction were pumped by means of a Toepler pump into a portable mercury gas holder, and transferred to a small-capacity

* Work is at present in progress on reactions photosensitized by $Cd(5^1P_1)$ atoms, using the resonance line at 2288A.

TABLE I. *Gaseous products of the reaction. Temperature = 310°C, trap temperature = −80°C, apparent volume of system = 1965 cc, propane pressure = ca. 10 cm, intensity of λ 3261 = ca. 6×10^{-6} Einstein per sec.*

Run No.	Saturator Temperature, °C	Time, hrs.	Initial Volumes		Volume of Gaseous Products, cc				Propane Consumed		H_2 Formed, cc per min.	$\frac{CH_4}{H_2}$ Formed
			C_3H_8, cc	H_2, cc	H_2	CH_4	C_3H_8	C_4H_{10}	cc per min.	Moles per sec. $\times 10^6$		
1	280	4	785	—	270	74	58	—	3.03	2.06	1.13	0.27
2	280	4	785	—	—	—	88	71	2.90	1.98	—	—
3	280	4	785	—	—	—	63	67	3.01	2.05	—	—
4	280	2	785	—	110	37	380	—	3.38	2.30	0.92	0.34
5	280	2	785	—	108	36	320	—	3.88	2.64	0.90	0.33
6	280	2	795	—	—	—	—	37	—	—	—	—
7	280	1	790	—	66	14	552	—	3.97	2.70	1.10	0.21
8	280	0.5	810	—	—	—	693	—	3.90	2.66	—	—
9	250	4	785	—	191	70	119	—	2.78	1.90	0.80	0.37
10	250	2	785	—	128	35	356	—	3.58	2.44	1.06	0.27
11	280	4	410	395	445	144	35	—	1.56	1.06	0.21	2.88
12	280	4	410	395	444	143	36	—	1.56	1.06	0.20	2.92
13	280	4	410	419	—	—	—	19	—	—	—	—
14	280	4	419	388	—	—	—	21	—	—	—	—
15	280	4	388	395	—	—	—	18	—	—	—	—
16	280	2	410	395	501	70	59	—	2.93	1.99	0.88	0.66
17	280	1	410	395	452	29	170	—	4.00	2.72	0.95	0.51
18	280	1	410	395	—	—	—	17	—	—	—	—
19	280	0.5	401	395	—	—	288	—	3.77	2.57	—	—

low temperature distillation apparatus of the Podbielniak type. Tests for unsaturates were made on all fractions by conventional methods.

The liquid products of the reaction were fractionated in a microdistillation apparatus.

The propane used was obtained in cylinders from the Ohio Chemical and Manufacturing Company. It was stated to be 99.8 percent pure, and no appreciable impurities could be detected with the analytical methods employed. It was therefore used without further purification.

Hydrogen was obtained from commercial cylinders. It was purified by passage over platinized asbestos at 700°C and through a liquid-air trap.

The absorption of cadmium resonance radiation

The interpretation of experiments on photosensitized reactions requires some knowledge of the quenching processes involved. In the case of hydrogen it is known from the work of Lipson and Mitchell[14] and of Olsen[15] that we have

$$Cd(^3P_1)+H_2=CdH+H,$$

and that the quenching cross section is 0.67×10^{-16} cm². This is considerably smaller than is the case with $Hg(^3P_1)$ atoms, but the actual quenching (i.e., the fractional diminution in the intensity of the fluorescent radiation at a given hydrogen pressure) is about the same on account of the fact that the life of the excited cadmium atom is about 20 times longer than that of mercury. No information is available on the quenching of excited cadmium atoms by propane, but the cross section is quite high in the case of mercury.[16,17] Measurements have been made, however, of the "absorption" of cadmium resonance radiation by propane.[6] These, of course, by no means give true information about quenching,[18] but they give a qualitative indication of the amount of radiation absorbed under various conditions of pressure, etc. Thus the following values were found for the "absorption" of λ3261 by propane and by hydrogen.

Thickness of absorbing layer 7.5 cm; cadmium vapor pressure *ca.* 0.018 mm; temperature 278°C.

Hydrogen

Pressure, mm	0.5	1.0	2.0	4.0	16.0	21.0	42.0
% absorbed	48	61	71	78	89	97	97

Propane

Pressure, mm	0.5	1.0	1.5	2.0	5.0	12.0	45.0
% absorbed	56	70	80	87	89	91	97

[14] H. C. Lipson and A. C. G. Mitchell, Phys. Rev. **48**, 625 (1935).
[15] L. Olsen, J. Chem. Phys. **6**, 307 (1938).
[16] J. R. Bates, J. Am. Chem. Soc. **52**, 3825 (1930).
[17] J. R. Bates, J. Am. Chem. Soc. **54**, 569 (1932).
[18] See, for example, A. C. G. Mitchell and M. Zemansky, *Resonance Radiation and Excited Atoms* (London, 1934).

The indications thus are that propane quenches almost as strongly as hydrogen, and that at the pressures used in this work there will be almost complete absorption of λ3261.

Results

The results are given in Tables I–V. It should be noted that in all cases, with the exception of Table III, the trapping temperature was −80°C. The initial amount of propane in the system was always greater than the vapor pressure at this temperature (about 10 cm), and hence propane condensed in the trap and its partial pressure remained approximately constant at 10 cm as the run progressed. In a few of the longer runs, the propane consumption was high, and the propane was almost all consumed at the end. At the trapping temperature of −80°C, hexane and higher hydrocarbons were completely removed from the reaction system, and pentanes would have a vapor pressure of about 1 mm. Butane, however, would have a vapor pressure of about 9 mm, and hence would recirculate and could enter into secondary reactions to a considerable extent. Hydrogen and methane, of course, were entirely in the gas phase. The pressure change could not conveniently be used as a measure of the reaction, since a large part of the products and of the reactant were condensed in the trap. The reaction was therefore followed entirely by analysis. For experimental reasons, it was found to be convenient to transfer all the gaseous products of the reaction to the still using a Toepler pump and a portable gas-holder, while the trap was main-

TABLE II. *Liquid products of the reaction—material balance. Conditions as in Table I.*

Run No.	Saturator Temperature, °C	Time, Hours	Unaccounted for in Gaseous Products: Ratio H/C	Unaccounted for in Gaseous Products: Calculated as Gaseous C_6H_{14} on Basis of Carbon Unaccounted for, cc	Calculated as Liquid Hexane at 20°C, cc	Liquid Products Found, cc at 20°
1	280	4	2.34	305	1.62	—
2	280	4	—	—	—	1.45
3	280	4	—	—	—	1.38
4	280	2	2.43	173	0.92	—
5	280	2	2.47	203	1.08	—
6	280	2	—	—	—	0.88
7	280	1	2.45	105	0.56	—
8	280	0.5	—	—	—	—
9	250	4	2.41	275	1.47	—
10	250	2	2.44	185	0.99	—
11	280	4	2.35	150	0.85	—
12	280	4	2.35	150	0.85	—
13	280	4	—	—	—	0.68
14	280	4	—	—	—	0.70
15	280	4	—	—	—	0.62
16	280	2	2.35	157	0.89	—
17	280	1	2.44	112	0.64	—
18	280	1	—	—	—	0.43
19	280	0.5	—	—	—	—

TABLE III. *The effect of pressure. Saturator temperature = 280°C, time = 1 hour, trap temperature = 0°C, other conditions as in Table I.*

Propane Pressure, cm	Propane Consumed, Moles per sec. ×10⁶	Propane Pressure, cm	Propane Consumed, Moles per sec. ×10⁶
10.0	0.82	40.5	1.26
	0.80		1.09
20.6	1.18	60.4	1.06
	1.18		

TABLE IV. *Effect of saturator temperature. Light input = ca. 4×10^{-6} Einstein per sec., time = 4 hours, temperature of reaction vessel = 310°C.*

Saturator Temperature, °C	Vapor Pressure of Cadmium, mm*	Propane Reacting Moles per sec. ×10⁶
310	6.0×10^{-2}	1.85
280	1.8×10^{-2}	1.88, 1.70
265	1.0×10^{-2}	1.65
250	4.7×10^{-3}	1.42
225	1.4×10^{-3}	1.24
200	3.4×10^{-4}	0.36

* It is probable that the actual amount of cadmium vapor in the gas was less than these values.

TABLE V. *The liquid products.*

Runs with Propane Alone: Boiling Range, °C	Runs with Propane Alone: Weight Percent of Sample	Propane-Hydrogen Mixtures: Boiling Range, °C	Propane-Hydrogen Mixtures: Weight Percent of Sample	Remarks
32–35	16	34–43 (mainly 35)	10	Pentanes
53–60 (mainly *ca.* 58)	64	50–58 (mainly 56–58)	43	Hexanes
		60–78 (mainly 60–68)	5	
78–80	18	80–83 (mainly 80–82)	19	Heptanes
Higher	2	Higher	23	

tained at −80°C. Under these circumstances it was doubtful if all the butane could be recovered. For this reason only hydrogen, methane and propane were determined in some experiments, and separate runs under identical conditions were made for butane and liquid products. In these runs the products were pumped slowly out of the apparatus through a liquid-air trap, and the material condensed in the trap was transferred to the still.

Blank runs showed that the presence of cadmium (and traces of oxide) in the system at 280°C did not cause any appreciable catalytic decomposition of propane.

(1) Results with propane alone

The amounts of reaction are given in Table I for runs of various duration. The variation of propane consumption with time is shown in Fig. 1. It will be seen that in the early stages of the reaction, up to about 2 hours, the rate is independent of time and secondary reactions of the products are therefore negligible. The initial rate corresponds to about 4×10^{-6} mole of propane consumed per second, which is roughly equivalent to a quantum yield of 0.6.

The dependence of the rate on the propane pressure cannot be obtained from the data of Table I, so a few runs were made to determine this, the results of which are given in Table III. In these runs the trap was kept at 0°C. Under these circumstances hexane will be entirely in the gas phase (vapor pressure about 45 mm) and secondary reactions will be of importance. As a result the propane consumption at 10 cm pressure is definitely less than in the runs given in Table I. However the data of Table III show the general effect of increasing propane pressure. At higher pressures it will be seen that the propane consumption is independent of the propane pressure. At lower pressures the rate falls off, presumably owing to incomplete absorption of resonance radiation.

The effect of the temperature of the cadmium saturator is shown by runs 9 and 10 in Table I. By comparison with runs 1 to 8, these appear to indicate a slight falling off in rate when the temperature of saturation is reduced from 280° to 250°C. This point is better illustrated by a series of runs made especially for this purpose and given in Table IV. It will be seen that in the range 265° to 310°C the temperature of the saturator has little effect. At lower temperatures, however, the rate falls off because of the presence of insufficient cadmium vapor in the reaction system.

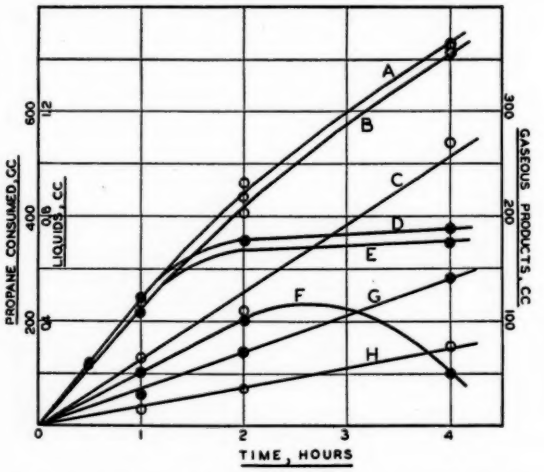

FIG. 1. ○ Runs with propane alone; ● runs with propane-hydrogen mixtures. (A) Propane consumption—propane alone; (B) liquid products—propane alone; (C) hydrogen production—propane alone; (D) propane consumption—propane-hydrogen mixtures; (E) liquid products—propane-hydrogen mixtures; (F) hydrogen production—propane-hydrogen mixtures; (G) methane production—propane-hydrogen mixtures; (H) methane production—propane alone.

The gaseous products of the reaction are also given in Table I, and consist of hydrogen, methane and butane. Traces of ethane were also detected. As shown by Fig. 1, in the early stages of the reaction the quantities of hydrogen and methane increase linearly with time. Towards the end of the reaction, the quantity of hydrogen increases somewhat faster. However, at this stage most of the propane has been consumed, and secondary reactions are coming into play to an increasing extent.

In Table II a material balance is given, and the amount of liquid products found is compared with the quantity of material otherwise unaccounted for. The hydrogen/carbon ratio of the unaccounted for material varies from 2.34 to 2.47. That for hexane is 2.33. In view of the large number of operations involved in a material balance, the agreement is as good as could be expected. A comparison of the last two columns shows that, on the average, the quantity of

liquid recovered is about 80 to 85 percent of the unaccounted for material. Considering the solubility of the higher boiling liquids in stopcock grease (Apiezon N grease was used), and the fact that a very small amount of carbonaceous material was formed in the saturator and connecting tubing, the agreement is excellent.

From Fig. 1 it will be seen that the formation of liquid products closely parallels the propane consumption. It appears, therefore, that the liquid products are a primary part of the reaction (i.e., are not formed by secondary reactions of *stable* substances).

The liquid products were fractionally distilled in a microstill of the Podbielniak type. The results of typical distillations are shown in Table V. It will be seen that the products consist mainly of hexanes, with smaller amounts of a lighter and a heavier fraction. As in the case of the mercury photosensitized reaction, the hexanes appear from their boiling points to be predominantly 2-Me-pentane and/or 2,3-di-Me-butane. The significance of this is discussed in the next section. The lighter fraction undoubtedly consists of pentanes (*n*-pentane boils at 36.1° and 2-Me-butane at 30.0°C). The only possibilities for the heavier fraction would appear to be some of the heptanes, *viz.* 2,2-di-Me-pentane (b.p. 78.9°), 2,4-di-Me-pentane (80.8°), 3,3-di-Me-pentane (86.0°), and 2,2,3-tri-Me-butane (80.8°). This question is discussed further later. Inasmuch as pentanes and heptanes are present, the material balance, etc., in Table II is somewhat inaccurate since it is constructed on the assumption that the liquid products are exclusively hexanes. However, since the balance is in any case only approximate, and since pentanes and heptanes are present in approximately equal amounts, no appreciable change would be introduced if the more laborious calculation were made.

(2) Results with propane-hydrogen mixtures

Experiments on the rate of reaction are given in Table I and Fig. 1. It will be noted that in the early stages of the reaction the rate of propane consumption is the same in the presence or in the absence of hydrogen, i.e., about 4×10^{-6} mole of propane is consumed per second. In the later stages of the reaction, the propane consumption falls below that for propane alone merely because less propane is present in the system and its consumption is approaching completion.

The gaseous products of the reaction, also shown in Table I, are qualitatively similar to those found with propane alone. Quantitatively, in runs of short duration the products are not greatly different. Thus, comparing runs 7 and 17, we have a hydrogen consumption of 1.10 and 0.95 cc per min., respectively, rather more methane in run 17, and, by extrapolation, less butane. In longer runs these differences are exaggerated, and the hydrogen formation becomes relatively much less and the methane formation much greater. The general trend of the products with time is shown by Fig. 1.

From Table II and Fig. 1, it will be seen that the amount of liquid products formed closely parallels the propane consumption in runs in the presence and in the absence of hydrogen. Further, from the data of Table V, and from the material balance in Table II, the liquid products appear to be very similar in nature, the only difference being that in the presence of hydrogen there is an increase in the amount of higher boiling products, mainly at the expense of hexanes.

Discussion

The only previous work on the cadmium photosensitized reactions of propane is that of Steacie and Potvin,[6] who made one run in the course of another investigation. Their general results were the same, but they found much more methane than hydrogen. The difference is undoubtedly due to the fact that in their work the higher boiling products of the reaction were not trapped out, and hence secondary reactions of hexane, etc., predominated.

The primary reaction

In the case of the mercury photosensitized reaction, the primary process is unquestionably

$$Hg(^3P_1)+C_3H_8=Hg(^1S_0)+C_3H_7+H \quad (10a)$$

or

$$Hg(^3P_1)+C_3H_8=HgH+C_3H_7, \quad (10b)$$

the ultimate result in both cases being a C−H bond split to yield C_3H_7 and H. In view of the

products found here, there seems to be no doubt that we again have a C−H bond split. As discussed previously in the case of ethane, there is no question that the C−H bond strength is greater than the excitation energy of $Cd(5^3P_1)$, *viz.* 87.3 kcal. Hence the primary process must be

$$Cd(^3P_1)+C_3H_8=CdH+C_3H_7, \qquad (15)$$

followed by

$$CdH=Cd(^1S_0)+H. \qquad (16)$$

This gives as the upper limit for the C−H bond in propane a value of 87.3+15.5=102.8 kcal., plus, perhaps, a small contribution from the thermal energy of the molecules.

In the presence of hydrogen the rate of consumption of propane is the same, and the products are not sensibly altered. We must have as a primary process, in addition to (10),

$$Cd(^3P_1)+H_2=CdH+H, \qquad (17)$$

followed by

$$H+C_3H_8=C_3H_7+H_2. \qquad (1)$$

The identity of the rates in the two cases is strong evidence for this, since the sequences (15), (16), (1) and (17), (16), (1), both correspond to the same over-all result, *viz.*

$$2C_3H_8+Cd(^3P_1)=2C_3H_7+H_2+Cd(^1S_0).$$

The primary step appears, therefore, to be established as the same as that with mercury photosensitization.

True secondary reactions

In view of the large yield of hexane and hydrogen, the main secondary reactions must be

$$H+C_3H_8=C_3H_7+H_2, \qquad (1)$$

$$2C_3H_7=C_6H_{14}. \qquad (12)$$

However, even in experiments of short duration, methane and butane appear as products. These can most simply be accounted for by

$$H+C_3H_7=C_2H_5+CH_3, \qquad (2)$$

$$CH_3+C_3H_8=CH_4+C_3H_7, \qquad (18)$$

$$CH_3+C_3H_7=C_4H_{10}, \qquad (19)$$

$$2C_2H_5=C_4H_{10}. \qquad (20)$$

Reaction (18) is known to occur at this temperature from the work of Smith and Taylor.[19] Reaction (2) is of the "atomic cracking" type,[20] and the evidence for its occurrence has already been discussed. Recombination reactions such as (19) and (20) are generally considered to have a very low activation energy.[21] The formation of pentane can also be accounted for by recombination,

$$C_2H_5+C_3H_7=C_5H_{12}. \qquad (21)$$

At the temperatures under consideration the propyl radical is unstable and will decompose to some extent, yielding the sequence

$$C_3H_7=C_2H_4+CH_3, \qquad (5)$$

$$R+C_2H_4=\text{alkyl radical}, \qquad (22)$$

(where R=H, CH_3, C_2H_5, etc.).

The multiplicity of secondary reactions makes the whole process highly complex. However the preponderance of hexane and hydrogen in the products means that the main course of events is extremely simple, and involves only reactions (1) and (12). These should proceed readily, since (1) has an activation energy of only 10 kcal.,[10,11] and (12) should have a low activation energy in conformity with other recombination reactions.

The reaction

$$C_3H_7+C_3H_8=C_6H_{14}+H \qquad (23)$$

cannot be suggested as a source of hexane. It is of the same general type as

$$CH_3+CH_4=C_2H_6+H. \qquad (24)$$

The reverse of this

$$H+C_2H_6=CH_4+CH_3 \qquad (25)$$

has been the subject of much discussion[10–12, 20, 22, 23] and it is generally accepted that reaction (25) has a very high activation energy, of the order of 30 kcal. Now reaction (25) involves breaking a C−C and forming a C−H bond, and should

[19] J. O. Smith and H. S. Taylor, J. Chem. Phys. **7**, 390 (1939).
[20] F. O. Rice and E. Teller, J. Chem. Phys. **6**, 489 (1938).
[21] J. C. Jungers and H. S. Taylor, J. Chem. Phys. **6**, 325 (1938).
[22] E. Gorin, W. Kauzmann, J. Walter and H. Eyring, J. Chem. Phys. **7**, 633 (1939).
[23] H. S. Taylor, J. Phys. Chem. **42**, 763 (1938).

therefore be exothermic to the extent of 10 to 20 kcal. Hence, if it has an activation energy of 30 kcal., the reverse reaction, (24), must have an activation energy of 40 to 50 kcal., which rules it out entirely as a possible step.

Secondary reactions of the products

In the presence of hydrogen there is an increase in methane production and a decrease in butane. This is especially marked towards the end of the reaction when the propane concentration is approaching zero. There seems to be no doubt that the effect is due in part to the attack of butane by hydrogen atoms, since this is known to produce methane.[12] A further cause is undoubtedly the attack of pentane by hydrogen atoms, since pentane is not efficiently trapped out under the experimental conditions employed. The increase in higher boiling products in the presence of hydrogen is undoubtedly due to C—C bond splitting by reactions of the "atomic cracking" type.

The liquid products of the reaction

As in the case of mercury photosensitization, the hexanes formed appear from their boiling points to be mainly 2,3-di-Me-butane and 2-Me-pentane. This again indicates that the radicals formed are mainly isopropyl rather than *n*-propyl, since no indications of the presence of *n*-hexane were obtained. This is in agreement with the work of Smith and Taylor which indicates that secondary hydrogen atoms are less strongly bound than primary, to the extent of about 2.8 kcal. Since there are 6 primary to 2 secondary hydrogens in propane, this would make the relative rates

$$\frac{\text{abstraction of secondary hydrogen}}{\text{abstraction of primary hydrogen}} = \frac{e^{2800/RT}}{3} = 3.8$$

at 300°C. This, neglecting steric factors, etc., would correspond to the formation of 2,3-di-Me-butane, 2-Me-pentane, and *n*-hexane in the proportions of roughly 16 : 4 : 1. This is entirely compatible with our results, since an amount of *n*-hexane as small as this would certainly have escaped detection.

From this point of view the small amount of liquid which boiled in the range 78° to 80°C is perhaps significant. There are no hexanes in this range, and the obvious possibilities are heptanes. The formation of heptane could well arise from the addition of a methyl radical to hexyl. If hexyl radicals are present we would expect them to arise by the abstraction of a hydrogen atom from hexane, and on the basis of Smith and Taylor's work we would expect the H atom thus removed to be a tertiary one. In this way from 2,3 di-Me-butane and 2-Me-pentane we would obtain, respectively, 2,2,3-tri-Me-butane with a boiling point of 80.8° and 2,2-di-Me-pentane with a boiling point of 78.9°C. Both compounds therefore correspond to the boiling range found, and there is only one other heptane which is at all close to this range. The heptanes found are, therefore, entirely in accord with the arguments adduced above concerning the hexanes.

Comparison with the mercury photosensitized reaction

The results are fundamentally very similar to those obtained by mercury photosensitization. There is, however, one distinct difference. In the mercury photosensitized reaction, even at 300°C, other secondary reactions are negligible, and the products are *almost exclusively* hydrogen and hexanes. In the cadmium photosensitized reaction the products are predominantly the same, but methane, butane, and pentanes are also formed in considerable amount. Once methyl radicals are formed butane and pentane production is to be expected, and hence the main difference appears to be the presence of hydrocarbon chain splitting in the case of the cadmium photosensitized reaction. Apparently then, either

$$H + C_3H_7 = C_2H_5 + CH_3 \qquad (2)$$

or

$$C_3H_7 = C_2H_4 + CH_3 \qquad (5)$$

is more pronounced in this case. The light intensity used here is considerably less than that used in the case of mercury. On the other hand the cadmium vapor pressure used is considerably higher than that used with mercury. This would tend to concentrate the reaction into a portion of the vessel nearest to the lamp. The two influences therefore compensate one another, and the radical concentrations, etc., cannot be

very different. It is therefore difficult to explain the differences in the results on the basis of differences in concentration.

A second possibility is that, on account of the concentration of the reaction zone around the lamp, surface effects come into play, especially the catalytic decomposition of the propyl radical. However, a fourfold variation in the cadmium vapor pressure produced no noticeable effect, and this renders such an explanation unlikely.

There remains one other, rather interesting, possibility. In the case of mercury photosensitization the evidence[16] is somewhat against the formation of HgH as an intermediate in the primary process. In the cadmium reaction CdH must be formed for energetic reasons. Furthermore, CdH has a much higher heat of formation (15.3 kcal.) than HgH, and hence it will have an appreciable life even at 300°C (about 10^{-7} sec.). This raises the possibility of reactions of CdH occurring more readily than the corresponding reaction with H atoms, such as

$$CdH+C_3H_8=CH_4+C_2H_5+Cd.$$

This discussion is, of course, purely speculative, but the occurrence of reactions involving CdH is a definite possibility.

The authors wish to express their indebtedness to Mr. R. Maillet for his assistance during the course of this investigation.

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Infra-Red and Raman Spectra of Polyatomic Molecules

XIII. Nitromethane*

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The infra-red spectrum of gaseous nitromethane has been studied over the wave-length range from 3 to 25 μ. The Raman work of Pendl, Reitz and Sabathy has been checked. These data together with a partial normal coordinate treatment enable us to make an assignment of the observed lines and bands which accounts for all the fundamental frequencies except the torsion around the C−N bond. The fundamental frequencies for the gas are 476, 599, 647, 921, 1097, 1153, 1384, 1413, 1449, 1488, 1582, 2965, 3048 (2). No decision regarding the potential barrier restricting the internal rotation of the methyl group can be made until at least one thermodynamic quantity has been measured. The present results are compatible with the usual structure CH_3NO_2.

IN previous papers of this series[1] the vibration frequencies of a number of simple molecules have been obtained. Nitromethane was chosen for study next for several reasons. It is a substance of some industrial importance so that a knowledge of its thermodynamic properties would be desirable. Furthermore it is another example of a reasonably simple molecule in which the possibility of rotation of a group about a single bond exists. Finally, its Raman spectrum has been used as an argument for a structure different from the conventional one represented by the formula CH_3NO_2.

Experimental Part

Most of the experimental work was performed on a sample of nitromethane presented to us by the Commercial Solvents Corporation. The sample was purified in their laboratories by distillation through a 5′ by ¾″ Fenske column (reflux ratio 10 : 1). It distilled at constant temperature and gave no test for water with anhydrous copper sulfate. Certain preliminary work was performed on a sample purchased from the Eastman Kodak Company and redistilled by us.

The infra-red spectrometer has been described previously.[2] Fluorite, rocksalt, and potassium bromide prisms

* Part of this material was presented to the Division of Physical and Inorganic Chemistry of the American Chemical Society at Detroit, September, 1940.

† Harvard National Scholar.

[1] J. Chem. Phys., 1938–1940.

[2] H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. 6, 197 (1938).

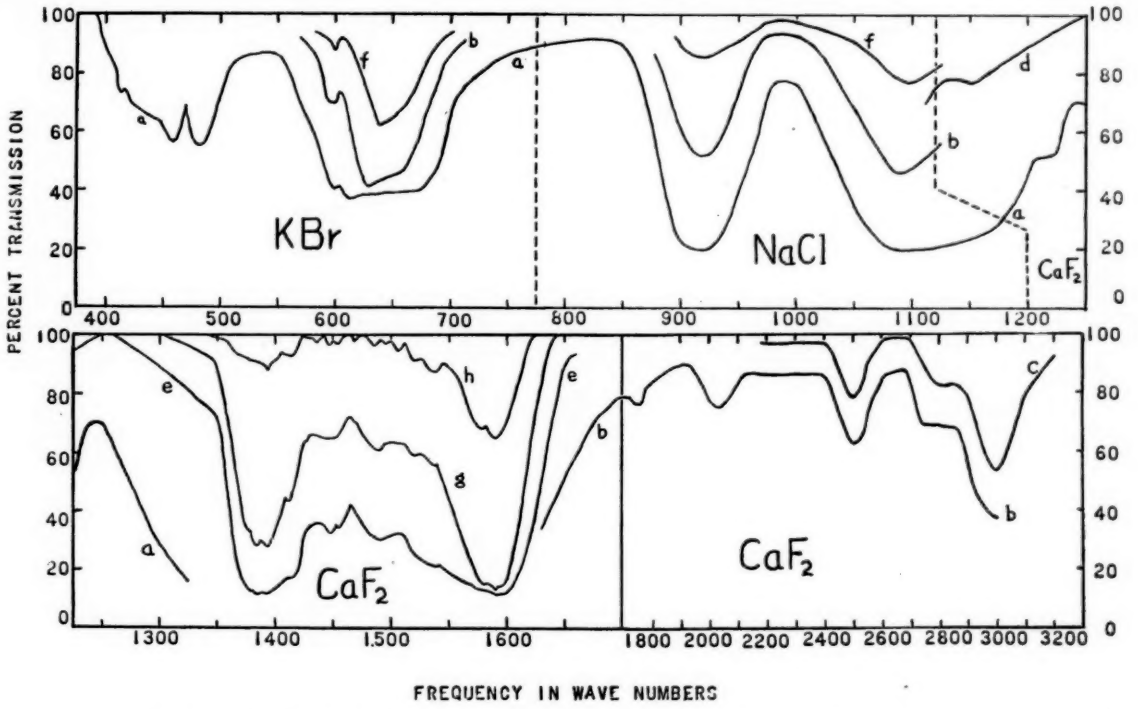

FIG. 1. The infra-red absorption spectrum of nitromethane. Curves *a* (760 mm), *b* (275 mm), and *c* (20 mm) were run in a heated cell 20 cm in length, the pressures being estimated roughly from the liquid temperature. Curves *d* (35 mm), *e* (20 mm), *f* (10 mm), and *g* (7 mm) were run in a 30-cm unheated cell. After running at 20 mm the cell was pumped for an hour with the oil pump. The residual nitromethane gave curve *h*.

were used in their appropriate spectral regions. Since it was necessary to heat the absorption cell in order to produce sizeable gas pressures of nitromethane (b.p., 101), a special cell was constructed consisting of a glass tube 20 cm long and 44 mm in diameter fitted with a side arm for holding the liquid sample. The glass was wrapped with thin copper sheeting to equalize the heating and was insulated with asbestos in which were imbedded the heating wires. The ends of the cell were fitted with detachable, heated collars made of heavy copper insulated on the outside. These collars extended 2 inches beyond the ends of the cell and served to prevent condensation of nitromethane on the cell windows. Two types of windows were used. Rocksalt windows cemented on with clear Glyptal gave fair results for vacuum-tight work. Care must be taken to bake the solvent out of the Glyptal before filling the cell, or solvent bands will show in the spectrum. Once the Glyptal has been baked and hardened it is necessary to keep the cell at constant temperature in order not to break the salt windows. The nitromethane pressure is varied by varying the temperature of the liquid in the side arm. If it is not essential to keep air out of the cell, it is convenient to use thin resin films for windows.[3] Films of Duco cement about half a micron thick survive the high temperature (120°) and prevent the loss of undue amounts of sample. They may be heated and cooled at will and are easily replaced. Much of the work in the rocksalt and potassium bromide regions was done in a cell with KBr windows cemented on with Duco household cement. This cement remains flexible at the high temperature and thereby lessens the danger of cracking the windows, but since the cell was open to the air through a long condenser tube, the effect of vacuum on this cement over a long time at high temperature was not tested.

[3] A. J. Wells, J. App. Phys. **11**, 137 (1940).

The bands of nitromethane observed between 3 and 25μ at various pressures are plotted in Fig. 1. The numerical frequencies are listed in Table I along with an estimate of intensities.

TABLE I. *Frequencies of bands observed in the infra-red spectrum.*

FREQUENCY	INTENSITY	FREQUENCY	INTENSITY
476	medium	1488	weak
599	medium	1520	very weak
647	strong	1582	very strong
921	medium	~1680	doubtful and very weak
1097	medium	1760	very weak
1153	weak	2035	weak
~1205	very weak	2500	medium
1384	very strong	~2800	weak
1413	weak	2995	medium strong
1449	weak		

TABLE II. *Raman data of Pendl, Reitz and Sabathy.*

SHIFT	INTENSITY	DEPOLARIZATION FACTOR	COINCIDENT INFRA-RED BAND
480	8	0.89	476
608	3	*dp*	599
656	10	.40	647
915	12	.07	921
1096	3	.74	1097
1314	2	*dp*	none
1333			
1374	7	.33	1384
1403	8	.41	1413
1558	5	.81	1582
2766	1	—	~2800
2965	10	.09	2995
3048	3	.96	

The infra-red spectrum of the gas has not been previously measured. Coblentz, Daniels, and Plyler and Burdine[4] have measured the infra-red spectrum of the liquid over various ranges from 1 to 14μ. Except for the copious number of bands found by Coblentz the agreement from 3 to 14μ is satisfactory. Our bands at 476, 599, 647, 1413, 1449, 1488, 1520, and the doubtful shoulder at 1680 are new.

The Raman spectrum of liquid nitromethane has been studied many times.[5] The polarization has been studied by Pendl, Reitz, and Sabathy whose data are reproduced in Table II. Using the Raman spectrograph in our laboratory[6] and the Polaroid method of obtaining qualitative polarization[7] data, we were able to verify their results except their weak lines at 1314 and 1333. In agreement with the earlier workers we find that their 1096 line is nearer 1105, and on many of our microphotometer curves it appears doubled with a separation of about 10 wave numbers. This is not apparent on the plates themselves, however. In order to eliminate excitation from the 4047 line of mercury we used a Wratten 2A gelatin filter. One thickness of such a filter cuts the violet line until it is barely visible on the plate while transmitting about 85 percent of the 4358 line. A combination of this filter with an alcohol solution of 90 milligrams per liter Rhodamine 5 G D N Extra (Du Pont)[7] gives a spectrum excited only by *e*, *f*, and *g*. In some experiments the background was reduced to a minimum by the use of a Wratten filter (experimental No. 846, presented to us by the Eastman Kodak Company) placed between the Raman tube and the spectrograph slit. This filter reduced the intensity of the 4358 line but left the Raman lines relatively unaffected.

THEORETICAL PART

The electron diffraction results[8] indicate that nitromethane has a tetrahedral structure. It is of interest to see how well the spectrum can be explained on this basis. When the methyl group is oriented at random with respect to the nitro group, the molecule possesses no symmetry. The most favorable orientation produces only one plane of symmetry. However, it has been shown[9] that when the force constants for cross terms such as those involving N−C−H and C−N−O

TABLE III. *Molecular vibrations of nitromethane.*

SYMMETRY CLASS	NUMBER OF VIBRATIONS	SELECTION RULES	DESCRIPTION OF MOTIONS	ASSIGNMENTS
A_1	5 Totally symmetrical	I.-R. Ra. (*P*)	CH_3 sym. stretching	2965
			CH_3 sym. bending	1413
			NO_2 sym. stretching	1384
			C−N stretching	921
			NO_2 sym. bending	647
A_2	1		Torsion about C−N	?
B_1	5 Parallel to plane of NO_2	I.-R. Ra. (*D*)	CH_3 unsym. stretching	3048
			NO_2 unsym. stretching	1582
			CH_3 unsym. bending	1449
			CH_3 rocking	1097
			NO_2 rocking	476
B_2	4 Perpendicular to plane	I.-R. Ra. (*D*)	CH_3 unsym. stretching	3048
			CH_3 unsym. bending	1488
			CH_3 rocking	1153
			NO_2 rocking	599

[4] Coblentz, "Investigations of infra-red spectra," Carnegie Institute Publication No. 35, Washington (1905). Daniels, J. Am. Chem. Soc. **47**, 2856 (1925). Plyler and Burdine, Phys. Rev. **35**, 605 (1930).

[5] Petrikaln and Hochberg, Zeits. f. physik. Chemie **B3**, 217 and 405 (1929). Ganesan and Venkateswaran, Ind. J. Phys. **4**, 196 (1929). Dadieu and Kohlrausch, Akad. Wiss. Wien **139**, 77 (1930) [reprinted in Monats. f. Chemie **55**, 379 (1930)]. L. Medard, J. chim. phys. **32**, 136 (1935). Pendl, Reitz and Sabathy, Proc. Ind. Acad. Sci. **8**, 508 (1938) [Raman jubilee volume].

[6] H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. **6**, 27 (1938).

[7] J. T. Edsall and E. B. Wilson, Jr., J. Chem. Phys. **6**, 12 (1938).

[8] Brockway, Beach and Pauling, J. Am. Chem. Soc. **55**, 2693 (1935), give the following dimensions:

C−N	1.46±0.02A
N−O	1.21±0.02A
O−N−O	127°±3°.

We assume that the C−H bond is 1.08A, and that the methyl group angles are tetrahedral.

[9] B. L. Crawford, Jr., and E. Bright Wilson, Jr., J. Chem. Phys. **9**, 323 (1941).

angles are treated as constants independent of the angle of twist about the C−N bond, or restricted to be certain functions of this angle, the secular equation can be factored as if the molecule possessed the symmetry C_{2v} (i.e., that of the nitro group alone). The details of the factoring will be published separately,[9] only the results being used here. Table III shows how this factoring divides the fifteen normal modes into the four classes of C_{2v}.

The selection rules and descriptions of the motion are given in columns three and four, and column five gives the best final assignment as explained below. Since thermodynamic calculations are based upon frequencies in the gas phase, we report our final assignment as coincident with the infra-red (gas) results, using the Raman data (liquid) only where the infra-red results are incomplete.

We can assign the A_1 class immediately on the basis of the polarization data. 2965 is the symmetrical hydrogen stretching frequency and 921 the carbon-nitrogen bond frequency as we should expect. We know 647 is the symmetrical bending of the nitro group by analogy with nitrogen dioxide. The polarized doublet around 1400 is caused by the symmetrical nitro group stretching motion united with the symmetrical bending of the methyl group. It is difficult to tell which motion is which since they are probably mixed in the normal modes.

In class B_1 the very strong infra-red band and depolarized Raman line around 1570 belong to the unsymmetrical stretching of the nitro group. The rocking motions of the nitro group would give rise to depolarized Raman lines of low frequency; namely 608 and 480. The moment of inertia of NO_2 about an axis perpendicular to its plane is about fourteen times as large as the moment about an axis lying in its plane and perpendicular to the symmetry axis, both axes passing through the center of gravity of the NO_2 group. Therefore we take the lower of the two frequencies as the in-plane rock leaving 600 for the analogous B_2 motion. When the infra-red band envelopes are calculated from the moments of inertia according to the method of Badger and Zumwalt[10] we find that B_1 bands should be doublets while B_2 bands should possess Q branches. Thus the assignment of these rocking motions is checked by the observed band envelopes (see Fig. 1). It is interesting that the B_1 band at 1582 also shows doublet structure. The broad, depolarized Raman band at 3048 is undoubtedly composed of the unsymmetrical hydrogen stretching frequencies of B_1 and B_2.

TABLE IV.

Class	Calculated	Observed
B_1	476	476
	1096	1097
	1456	1449
	1589	1582
B_2	596	599
	1157	1153
	1483	1488

TABLE V.

NCH bending constant	Methyl Rocking Frequencies	Splitting
0.55×10^5	1045	45 cm^{-1}
	990	
0.60×10^5	1080	46 cm^{-1}
	1034	
0.67×10^5	1134	53 cm^{-1}
	1081	
0.70×10^5	1157	61 cm^{-1}
	1096	

We have now assigned all the normal modes except the two unsymmetrical bending and the two rocking motions of the methyl group, and the torsion frequency. No evidence was found of the torsional frequency in either spectrum. The evidence still available for these assignments consists of the Raman lines at 1096, 1314 and 1333 and the infra-red bands at 1097, 1153, 1205, 1449, 1488, and 1520. In order to help differentiate between overtones and fundamentals, and in order to study the forces in the molecule, we resorted to a normal coordinate treatment for the B_1 and B_2 frequencies only. Our procedure was to choose force constants for the nitro group which fitted the experimental data. These were combined with Stitt's constants for the methyl group drawn from his work on ethane.[11] Then by changing from Stitt's value of 0.55×10^5 dynes/cm for the C−C−H angle constant to 0.70×10^5 dynes/cm for the N−C−H angle constant we were able to calculate frequencies which agreed very well ($\frac{1}{2}$ percent) with those observed, if we chose 1097 and 1153 for the methyl rocking frequencies and 1449 and 1488 for the unsymmetrical methyl bending frequencies. The results of the normal coordinate treatment for classes B_1 and B_2, the only classes calculated, are given in Table IV. Seven fre-

[10] Badger and Zumwalt, J. Chem. Phys. **6**, 711 (1938).

[11] F. Stitt, J. Chem. Phys. **7**, 297 (1939).

TABLE VI.

SPECTRUM	OBSERVED	ASSIGNMENT
Raman	1314	$2\times656=1312$
	1333	?
	2766	$1403+1374=2777$
Infra-red	~1205	$2\times599=1198$
	1520	$921+599=1520$
	~1680	$600+1097=1697$ (?)
	1760	$600+1153=1753$
	2035	$1384+647=2031$
	2500	$921+1582=2503$
	2800	$\{2\times1384=2768\}$ $\{2\times1413=2826\}$

quencies were calculated by adjusting only four constants, the rest being taken directly from Stitt.

The potential energy used corresponds to the appropriate parts of Stitt's potential III*h* for ethane with k_β(H−C−C) changed as mentioned above plus the following terms:

$$k_1(R_1-R_2)^2+k_2(\gamma_1-\gamma_2)^2+k_3\phi^2,$$

where R_1, R_2 are the displacements of the N−O distances, γ_1, γ_2 are the changes in the C−N−O angles, and ϕ is the change in the angle between the C−N bond and the NO_2 plane. The values found for the force constants are

$k_1=3.35\times10^5$ dyne/cm
$k_2=1.72\times10^{-11}$ dyne cm/radian^2
$k_3=0.240\times10^{-11}$ dyne cm/radian^2.

The method used to get the secular equation was that recently described.[9,12] The A_1 class was not calculated because it was not necessary for the assignment and because there were too many unknown force constants involved. However, an investigation of CD_3NO_2 is now under way which should make such a calculation feasible.

Except for the lack of symmetry in the nitro group we should expect the rocking and perpendicular bending frequencies of the methyl group to be degenerate as in ethane. Therefore it is interesting to study the splitting of these frequencies caused by the asymmetry of a neighboring group. We performed a series of calculations in which the bending constant of the N−C−H angle was varied while holding the constants internal to the methyl group fixed and also adjusting the nitro group constants to fit the observed frequencies, 476, 599 and 1582. In Table V we show how the splitting of the methyl rocking changed with the angle constant. The B_1 frequencies are the lower in each case. The fact that the splitting increases as the angle constant increases shows that the dominating influence in this frequency range is not the splitting in the nitro group rocking frequencies (476 and 599) but is the nitro group stretching frequency at 1582. Apparently this frequency interacts with the methyl rocking frequency in its symmetry class (B_1) in such a way as to reduce the latter, an effect which increases as the angle constant is raised. There is no B_2 frequency to depress the B_2 methyl rock, and the splitting therefore increases as shown.

A suggested assignment of overtones and combinations is given in Table VI. No assignment presents itself for the weak Raman shift of Pendl, Reitz and Sabathy[5] at 1333; and our assignment of the 1314 shift should give rise to a polarized line. Likewise the indicated assignment for the doubtful shoulder at 1680 violates the C_{2v} selection rules, a violation which might occur since the C_{2v} applies only approximately. There is some absorption centered around 1538 wave numbers which we think is the *R* branch of 1520 enhanced by the strong band at 1582.

In conclusion it is of interest to note that all of the fundamentals (except the torsion frequency) are observed in the infra-red, a very unusual situation for a molecule of this complexity. Furthermore all of the gas phase evidence and practically all of the liquid phase evidence is in agreement with the tetrahedral structure. Therefore we are inclined to doubt the "two form" hypothesis proposed by Pendl, Reitz and Sabathy.[5]

[12] E. B. Wilson, Jr., J. Chem. Phys. **7**, 1047 (1939).

Infra-Red and Raman Spectra of Polyatomic Molecules

XIV. Propylene

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The infra-red spectrum of gaseous propylene has been studied from 3 to 25μ with a spectrometer using fluorite, rocksalt and KBr prisms. A normal coordinate calculation of the fundamental frequencies has been made, using force constants obtained principally from ethylene and ethane. This information, when combined with the known Raman spectrum, permits an assignment of fifteen of the twenty fundamental frequencies and puts limits on four of the remaining frequencies.

THE question of the potential barrier restricting the internal rotation of the methyl group in propylene has attracted considerable attention in recent years.[1] A knowledge of the fundamental frequencies of vibration is important in the solution of this problem. Consequently we have examined the infra-red absorption spectrum of gaseous propylene and have studied the dynamics of the molecule in an effort to determine the vibration frequencies. As a result we believe that all but five of the frequencies have been located and that limits have been placed on the others.

EXPERIMENTAL RESULTS

The material was given to us by Professor G. B. Kistiakowsky, and was a special sample from the Linde Air Products Company with a stated purity of 99.9 percent. It was used without further purification. The spectrometer has been described in an earlier paper,[2] although as of this writing it has been improved by the addition of a third prism (fluorite), new slits, and by the introduction of a more sensitive thermocouple. The absorption curve is given in Fig. 1. In Table I a list of the frequencies of the band centers is given along with an estimate of the intensities and a list of Ananthakrishnan's Raman data.[3] The main regions of absorption are shown quite clearly in Fig. 1, but the choice of band centers involved some rather arbitrary decisions. This is particularly true from 1100 to 1500 wave numbers, the region of high resolution for the fluorite prism. At least five fundamentals, which must partly overlap, are expected in this region. The band at 919 is broader than we

TABLE I. *The infra-red spectrum of propylene gas.*

FREQUENCY IN CM^{-1}	INTENSITY	RAMAN SPECTRUM[3]
417	medium	432 *P* 3
578	strong	580 *D* ½*bd*
755	weak	
919	strong	920 *P* 6
~996	weak	
1166	weak	
1224	medium	
1244	weak	
1287, 1317	weak	1297 *P* 10
1399	weak	
1416	weak	1415 *P* 4
1448	strong	1448* weak
1472	medium	
1489, 1508, 1520	very weak	
1647	strong	1648 *P* 10*s*
1718	weak	
1830	medium	
1976	very weak	
2035	weak	
2320	weak	
2574	weak	
		2732 *P* 1
		2763 00
		2795 0
		2823 *P* ½
		2857 *P* 1
		2890 *P* 4
		2924 *P* 10
		2956 0
2994	strong	2990 *P* 1
		3010 *P* 6*b*
		3087 ½

* This shift is taken from the work of Bourguel and Piaux, reference 5. Apparently Ananthakrishnan failed to find it.

* Harvard National Scholar.

[1] (a) K. S. Pitzer, Chem. Rev. **27**, 39 (1940). (b) Crawford, Kistiakowsky, Rice, Wells and Wilson, J. Am. Chem. Soc. **61**, 2908 (1939). (c) T. M. Powell and W. F. Giauque, J. Am. Chem. Soc. **61**, 2366 (1939).

[2] H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. **6**, 197 (1938).

[3] R. Ananthakrishnan, Proc. Ind. Acad. Sci. **3A**, 527 (1936).

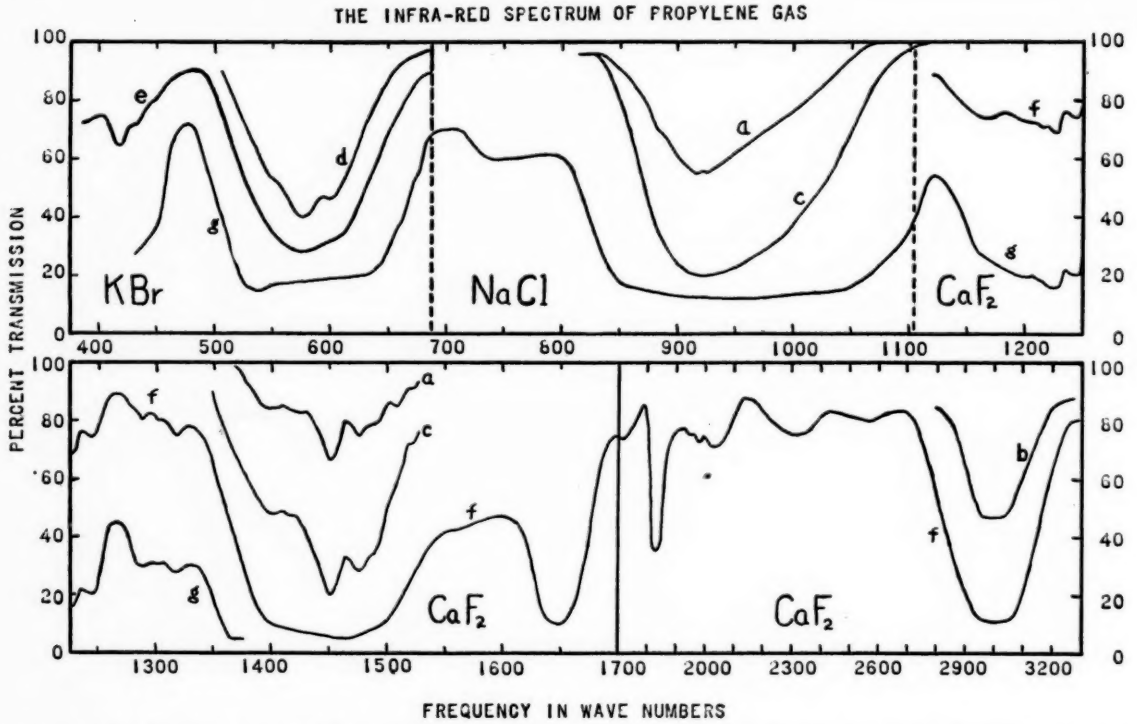

FIG. 1. The infra-red absorption spectrum of propylene gas. The transmission curves were taken in 30-cm glass cells using NaCl and KBr windows with gas at the following pressures: *a*, 10 mm; *b*, 12 mm; *c*, 52 mm; *d*, 80 mm; *e*, 170 mm; *f*, 189 mm; and *g*, 740 mm.

should expect for a single fundamental of this molecule and we therefore postulate a weaker band somewhere near 996 to account for the broad wing on the high frequency side.* The band at 417 cm^{-1} does not agree well with the Raman shift (for the liquid) of 432 cm^{-1}. Perhaps the center of the band is really at 432, where there is an inflection on the curve, but if so it is difficult to account for the shape of the band.

Bonner and Hofstadter[4] report a study of the infra-red spectrum of propylene from 1 to 15.5μ using only a rocksalt prism. Their results agree reasonably well with ours. Bourguel and Piaux[5] also measured the Raman spectrum of propylene, but they report no polarization data.

CALCULATION OF FREQUENCIES

Propylene, if one of the methyl hydrogen atoms is in the plane of the carbon atoms, possesses a plane of symmetry. Therefore in our normal coordinate treatment we used this orientation.[6] With one plane of symmetry the problem divides into fourteen in-plane and seven out-of-plane frequencies. By setting the C−H stretching constants equal to infinity and the C−C torsion constant equal to zero the problem is further reduced to ninth- and fifth-degree secular equations without significant loss of accuracy. For the methyl end of the molecule we used the ethane force constants of Stitt.[7] In our choice of the rest of the force constants we were guided by the results for ethylene, about which, however, there has been considerable doubt. In our first calculation we used an assignment suggested by Linnett[8] except that we raised the double bond twisting constant to fit the 578 frequency of propylene. After the publication of

* Since submitting this manuscript, we have been able to resolve this band and find a weak absorption center at 995 cm^{-1}.

[4] Bonner and Hofstadter, Phys. Rev. **52**, 249 (1937), abstract only.

[5] M. Bourguel and L. Piaux, Bull. soc. chim. [5] **2**, 1958 (1935).

[6] It has been shown that the orientation chosen has no effect on the results if certain approximations are made. See B. L. Crawford, Jr. and E. B. Wilson, Jr., J. Chem. Phys. **9**, 323 (1941).

[7] F. Stitt, J. Chem. Phys. **7**, 297 (1939). Potential function *III h*.

[8] J. W. Linnett, unpublished work (1938).

Conn and Sutherland's[9] assignment, we recalculated the out-of-plane frequencies using constants derived from their work on C_2H_4 and C_2D_4, except for the twisting constant. The latter constant was based on the value of about 820 cm^{-1} suggested to us for the C_2H_4 twist frequency by Eyster.[10]

Lists of the ethylene force constants are given in Table II; the reader is referred to Stitt's original paper for his work. In Table III we give the force constants actually used in the propylene calculation, which differed from the ethylene values in some cases because of different bond distances, etc. In Table IV are given the calculated frequencies from both calculations, a rough description of the types of motion, and the observed frequencies with which the calculation is to be correlated.*

TABLE II. *Ethylene force constants.* (C–H *stretching constants, which were later set equal to infinity, are not considered here.*)

CONSTANT	LINNETT	CONN AND SUTHERLAND‡	UNITS
C=C stretch	9.72	9.87	10^5 dynes/cm
C=C–H angle	0.939	1.000	10^{-11} dyne cm/radian^2
angle between C=C and plane of CH_2	0.2795	0.260	10^{-11} dyne cm/radian^2
twist angle	0.276	0.248	10^{-11} dyne cm/radian^2
Interaction constants between:			
C=C stretch and C=C–H angle	0.660	2.0	10^{-3} dynes/radian
C=C–H angles at same end	0.686	0.8986	10^{-11} dyne cm/radian^2
C=C–H angles on same side	0.000	0.2898	10^{-11} dyne cm/radian^2
C=C–H angles diagonally opposite	0.000	0.0340	10^{-11} dyne cm/radian^2
the two angles formed by C=C and CH_2 planes	0.000	0.1040	10^{-11} dyne cm/radian^2

‡ These constants were calculated by us from the assignment of Conn and Sutherland (reference 9) using their data for both C_2H_4 and C_2D_4.

[9] G. K. T. Conn and G. B. B. M. Sutherland, Proc. Roy. Soc. **A172**, 172 (1939).

[10] E. H. Eyster, private communication. See also the recent note: Burcik, Eyster and Yost, J. Chem. Phys. **9**, 118 (1941).

* The details of the normal coordinate treatment are being included in a thesis entitled "Studies in the infra-red" to be submitted to the Faculty of Arts and Sciences, Harvard University, by A. J. Wells.

ASSIGNMENT OF FREQUENCIES

In assigning the fundamental frequencies, it is convenient to consider first modes in which the motion is primarily along the minor axis of inertia. Below 2000 cm^{-1} there are five such frequencies which should be strong and polarized in the Raman effect. Three of them are undoubtedly the C–C stretch at 919, the C=C stretch at 1648, and the central C–H wag at 1297.[11] Also we are reasonably certain that the

TABLE III. *Force constants used in propylene.*

MAIN FORCE CONSTANTS	1ST CALC.	2ND CALC.	UNITS
In-plane:			
C–C bond	4.50		10^5 dynes/cm
C=C bond	9.72		10^5 dynes/cm
C–C–H ∠ in CH_3	0.64	same	10^{-11} dyne cm/radian^2
H–C–H ∠ in CH_3	0.535		10^{-11} dyne cm/radian^2
C=C–H ∠	0.939		10^{-11} dyne cm/radian^2
C–C=C ∠	1.20		10^{-11} dyne cm/radian^2
Out-of-plane:			
∠ between C=C and CH_2 plane	0.2795	0.26	10^{-11} dyne cm/radian^2
∠ between C=C and =C(H)(C) plane	0.31	0.29	10^{-11} dyne cm/radian^2
∠ of twist about C=C	0.41	0.36	10^{-11} dyne cm/radian^2
Interaction constants between:			
In-plane:			
C=C and C=C–H ∠	0.66		10^{-3} dynes/radian
C=C and C=C–C ∠	0.73		10^{-3} dynes/radian
both C=C–H ∠'s of CH_2	0.686		10^{-11} dyne cm/radian^2
C=C–C ∠ and adjacent C=C–H ∠	0.75	same	10^{-11} dyne cm/radian^2
For the CH_3 group: Stitt's $K_{c\gamma} \times r_{CH}^2$ (see ref. 4)	−0.54		10^{-11} dyne cm/radian^2
C–C–H ∠ and adjacent H–C–H ∠	0.023		10^{-11} dyne cm/radian^2
Out-of-plane: ∠ formed by C=C and CH_2 plane, and ∠ formed by C=C and =C(H)(C) plane	0.00	0.11	10^{-11} dyne cm/radian^2

[11] Bourguel and Piaux, reference 5, after studying the Raman spectra of nineteen compounds containing the group $CH_2=CH-$ came to the conclusion that the frequencies 1295, 1415, 1640, 3000, and 3080 were characteristic of this group. They assigned all but 1295 which we assign on the basis of the calculation.

TABLE IV. *Frequencies calculated for propylene.*

TYPE OF MOTION	1ST CALC.	2ND CALC.	OBS.
In-plane:			
C−C stretching	917	—	919
C=C stretching	1681	—	1647
CH_3 sym. bending	1386	—	1399
CH_2 sym. bending	1429	—	1416
CH wagging	1297	—	1297
C=C−C bending	428	—	417
CH_3 unsym. bending	1471	—	1448
CH_3 rocking	1022	—	?
CH_2 rocking	1111	—	?
Out-of-plane:			
CH rocking }	{574	538	578
C=C twisting }	{940	898	?
CH_3 unsym. bending	1474	1481	1472
CH_3 rocking	1000	1030	?
CH_2 rocking	1100	976	?

infra-red centers at 1399 and 1416 mark the symmetrical CH_3 and CH_2 bending motions, respectively. In the plane but largely perpendicular to the minor axis (along the middle axis) are four frequencies below 2000. The weaker polarized line at 432 (417 in the infra-red) is assigned to the C−C=C bend, and the strong infra-red line at 1448 is assigned to the internal methyl bending motion in this direction. The reason for assigning the lower methyl bending frequency in the in-plane class is the same in this molecule as in nitromethane. See preceding paper. The in-plane CH_3 and CH_2 rocking frequencies are uncertain. There are five low out-of-plane frequencies. 1472 is the internal methyl group bending in this class, but again the rocking frequencies are uncertain. The other two frequencies involve the torsion of the double bond and the out-of-plane motion of the C−H group. The lower of these is certainly the strong infra-red band and weak depolarized Raman line at 578, while the upper one forms our fifth uncertain fundamental. We make no attempt to differentiate among the six C−H frequencies at 2900–3100 cm^{-1}; they account for the numerous Raman lines observed in the vicinity. Fox and Martin[12] have studied this region of the infra-red in considerable detail and have been able to assign the observed frequencies to various parts of the molecule.

As possible assignments for our five uncertain frequencies we have no Raman shifts, a weak infra-red band at 755, the possibility of absorption centered around 996, a band at 1166, and a complicated region of absorption centered around 1224. The calculations indicate that the rocking frequencies should lie between 950 and 1150. Yet it is difficult to account for the complex band near 1224 on a combination-overtone hypothesis. The most likely assignment at the present time is that the 996 absorption is caused by CH_2 rocking while that at 1166 is caused by CH_3 rocking. The latter band, however, could be the first overtone of 578. Dr. W. W. Rice informs us that the assignment of 755 as the higher member of the C=C twisting-CH rocking combination gives poor agreement with the heat capacity data while an assignment around 900, in agreement with the calculation, leads to much more consistent results. The band at 755 may be a combination involving the unknown C−C torsion frequency; e.g., 578+177=755.

In conclusion it should be noted that the above remarks do not affect in any serious way the provisional assignment previously used[1b] for the calculation of the height of the barrier restricting free internal rotation in propylene. Although our knowledge at this time is still incomplete, we feel the evidence points to the high value of about 2100 calories per mole for the barrier.

[12] J. J. Fox and A. E. Martin, Proc. Roy. Soc. **A175**, 208 (1940).

The Normal Vibrations of Molecules with Internal Torsional Motions

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The vibrational problem has been treated for molecules consisting of a framework to which are attached any number of symmetrical tops, such as methyl groups. Nitromethane, methyl alcohol, neopentane, etc. are examples. The vibrational problem can be separated from the internal torsional and over-all rotation if the potential function is restricted so that the vibrational frequencies are independent of the torsion angles. The separation is effected by carrying out the normal coordinate treatment in the usual manner using however the value zero for all force constants involving torsion angles. The frequencies will not depend on the particular equilibrium orientation assumed for the tops. Furthermore the secular equation for the vibrational problem can frequently be factored to a greater extent than is indicated by the symmetry of the rigid molecule. The vibrational selection rules are also discussed and shown to be similar to those for normal molecules.

THE study of molecular vibrations has progressed to such a point recently that molecules in which internal rotations or librations are possible are now being investigated. It is the purpose of this paper to develop a method of treating the vibrations of molecules which consist of a framework to which are attached a number of symmetrical groups (such as methyl groups).[1] Examples are CH_3OH, CH_3OCH_3, mesitylene, etc.

SEPARATION OF COORDINATES

With high barriers, internal librational degrees of freedom can be treated as vibrations, with harmonic potential functions. As the barrier is lowered, the amplitude increases and the error involved in this assumption becomes too great because the molecule spends more and more time in configurations where the potential energy is far from being harmonic. It is then much more convenient to choose a coordinate system in which the energy of libration can be approximately separated from the vibrational energy and treated independently. In other words it becomes more important to take into account the nonparabolic shape of the potential energy than to treat accurately the interaction of the libration with the other vibrations.

The Sayvetz conditions

Sayvetz[2] has shown that, in order to separate the kinetic energy, coordinates should be used which cause the vanishing of the constant parts of the coefficients of the cross terms between vibrational and librational velocities. This provides a new condition with which to define these coordinates, which are measured in a rotating system of axes moving with the top relative to the main molecular axes.

In order to find these coupling terms and therefore the conditions above, the vectorial method is very convenient and follows very closely that employed for normal molecules.[3] The velocity of the kth atom in the mth top is the vector

$$\dot{\mathbf{R}}+\boldsymbol{\omega}\times\mathbf{r}_{mk}+\boldsymbol{\omega}_m\times\mathbf{s}_{mk}+\mathbf{v}_{mk}. \qquad (1)$$

Here $\dot{\mathbf{R}}$ is the velocity of the center of gravity of the molecule, $\boldsymbol{\omega}$ is the angular velocity of the framework axes, $\mathbf{r}_{mk}$ is the vector from the center of gravity to the atom, $\boldsymbol{\omega}_m$ is the angular velocity relative to the framework axes of the axes of the mth top, $\mathbf{s}_{mk}$ is the vector from the origin of

[1] The calculation of rotational partition functions for this class of molecules has been treated by L. S. Kassel, J. Chem. Phys. **4**, 276 (1936) (classical), and B. L. Crawford, Jr., J. Chem. Phys. **8**, 273 (1940) (quantum-mechanical treatment, including calculation of energy levels).

[2] A. Sayvetz, J. Chem. Phys. **7**, 383 (1939).

[3] E. B. Wilson, Jr. and J. B. Howard, J. Chem. Phys. **4**, 260 (1936).

the top axes to the atom, and $\mathbf{v}_{mk}$ is the velocity of the atom relative to the moving top axes.

When this vector is used to construct the kinetic energy in the usual way, a number of terms will occur, representing translational, rotational, internal rotational, and vibrational energies, plus coupling terms between them. Most of these coupling terms are eliminated or made small by applying the ordinary conditions which define the rotating framework axes, but there remain the following terms coupling vibration and internal rotation:

$$\sum_m \boldsymbol{\omega}_m \cdot \sum_k (m_{mk}\mathbf{s}_{mk} \times \mathbf{v}_{mk}), \tag{2}$$

in which m_{mk} is the mass of the atom mk.

The Sayvetz condition is equivalent to the vanishing of these terms, not as written, but when $\mathbf{s}_{mk}$ is replaced by $\mathbf{a}_{mk}$, the equilibrium value of $\mathbf{s}_{mk}$; i.e., the value of $\mathbf{s}_{mk}$ when there is no vibration. Furthermore the condition can be reduced to

$$(\sum_k m_{mk}\mathbf{a}_{mk} \times \boldsymbol{\varrho}_{mk})_\zeta = 0, \tag{3}$$

where $\boldsymbol{\varrho}_{mk}$ is the vector displacement of atom mk from its equilibrium position in the rotating top axes; i.e., $\boldsymbol{\varrho}_{mk} = \mathbf{s}_{mk} - \mathbf{a}_{mk}$. The subscript ζ indicates that the component along the symmetry axis of the top is involved, a result which follows from the fact that $\boldsymbol{\omega}_m$ lies along this axis.

Therefore the vibrational motions of the atoms of a top must not involve any component of vibrational angular momentum (to the first approximation) along the axis of the top; any such momentum is to be taken care of by the rotation of the top axes.

Choice of normal coordinates

We shall now show that if the molecule is treated as an ordinary rigid molecule, but all force constants involving the twist angles are put equal to zero, the above conditions are met. First think of a set of coordinates U_{lm} for each top m which are orthogonal linear combinations of the components of $(m_{mk})^{\frac{1}{2}}\boldsymbol{\varrho}_{mk}$, such that one U_{lm} for each m (say $l=l'$) has the form

$$U_{l'm} = K(\sum_k m_{mk}\mathbf{a}_{mk} \times \boldsymbol{\varrho}_{mk})_\zeta, \tag{4}$$

K being a normalizing constant. In terms of these coordinates the condition (3) is simply $U_{l'm}=0$ for each top m. If the normal coordinates Q_λ are thought of as linear combinations of the U's, the conditions will be satisfied if none of the Q_λ's involves $U_{l'm}$. If valence-type coordinates[4] are used in the actual solution of the vibrational problem, the normal coordinates obtained will be functions of these, so that we must arrange that none of the valence-type coordinates are functions of $U_{l'm}$ in order to insure that none of the Q_λ are functions of $U_{l'm}$. It is clear on examination of the valence-type coordinates that if a top is given a slight twist (corresponding to $U_{l'm}\neq 0$) the only valence-type coordinate affected is σ_m, the twist angle. Consequently if no normal coordinate is a function of σ_m, none will involve $U_{l'm}$ and Sayvetz's condition will be satisfied.

But it is shown in Appendix I that if the molecule is treated as an ordinary rigid molecule with a potential energy expressed in terms of valence type coordinates, and if the force constants (including cross-terms) which involve the twist angles are put equal to zero, none of the normal coordinates will involve the twist angles, except those of zero frequency. Consequently, Sayvetz's conditions will be satisfied. If the technique recently described[5] of treating the vibrational problem is used, the coordinates σ_m can be ignored from the beginning, since this is equivalent to putting its force constant equal to zero.

Separation of the potential energy

The preceding sections have shown how the kinetic energy may be approximately separated into a part depending on the normal coordinate velocities and a part depending on the librations. In order to solve the wave equation it is equally necessary that the potential energy separate.

Strictly speaking the potential energy is certainly not exactly separable. However, as an approximation it is probably satisfactory to

[4] Valence-type coordinates, that is changes in valence angles and in the lengths of valence bonds, are by far the most reasonable and useful coordinates for expressing the potential energy. The use of this set involves no loss in generality since as many cross terms as desired may be employed in the potential energy.

[5] E. B. Wilson, Jr., J. Chem. Phys. **7**, 1047 (1939); *ibid.* **9**, 76 (1941).

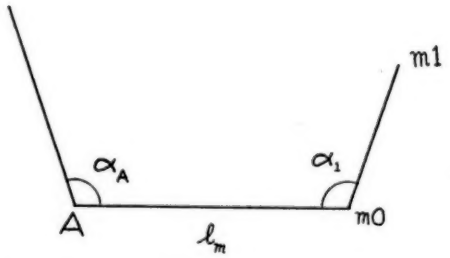

FIG. 1. Important bonds in the vicinity of the mth top. Atom ($m0$) is the central atom of the mth top, and atom ($m1$) some other atom of the top. Atom A is a framework atom, l_m being the axis bond for the mth top. The atom at the upper left may be either a framework atom or ($m'0$), the central atom of the m'th top.

assume that it is of the form

$$2V=\sum_{\lambda}\lambda_\lambda Q_\lambda^2+\sum_m f_m(\gamma_m). \tag{5}$$

Here $\lambda_\lambda=4\pi^2\nu_\lambda^2$ and the usual assumption of harmonic forces for the vibrations (but not for the librations) has been made. γ_m is the angle of the mth set of rotating top axes. Since it is defined in terms of the positions of axes and not of atoms, it differs slightly from the valence-type coordinate σ_m.

Constancy of vibration frequencies

It is also necessary to assume that the λ_λ are constants and not functions of γ. Actually this assumption is also an approximation but not a serious one. If desired, the small dependence of λ on γ could be treated as a perturbation. In order to obtain constant λ_λ, it is necessary and sufficient that there be a coordinate system in terms of which both the kinetic and potential energies have constant coefficients.

In terms of valence-type coordinates the kinetic energy of vibration is not independent of γ. To see that $2T$ depends on γ it is convenient to use the quantities

$$G_{jj'}=\sum_{m,k}(1/m_{mk})\mathbf{s}_{jmk}\cdot\mathbf{s}_{j'mk},$$

where the vectors $\mathbf{s}_{jmk}$ are the coefficients in the relations

$$R_j=\sum_{m,k}\mathbf{s}_{jmk}\cdot\boldsymbol{\varrho}_{mk}.$$

R_j is a valence-type coordinate and m_{mk} is the mass of atom mk. The quantities $G_{jj'}$ have been shown to be intimately related to the kinetic energy.[6] The vector $\mathbf{s}_{jmk}$ associated with a given coordinate R_j of a top and with the atom $m0$ of Fig. 1 will rotate relative to $\mathbf{s}_{j'm0}$ with $j'=\alpha_A$ so that the dot product $\mathbf{s}_{jm0}\cdot\mathbf{s}_{j'm0}$ will depend on γ.

However, it is possible to make linear combinations of the R's of the top such that the vectors associated with the combinations at atom $m0$ (and also at A) are directed either along the axis or perpendicular to it.[7] Furthermore since the top is symmetric, the combinations with vectors perpendicular to the axis of the top will occur in pairs such that their vectors are of equal length and at right angles to each other (degenerate pairs). The combination producing this result are the "internal symmetry coordinates," $\mathcal{R}_j$, for the top and reduce the group of symmetry operations of the top itself.

If we denote by $\mathcal{R}_a$ and $\mathcal{R}_b$ a degenerate pair of these coordinates, it is easy to see that the combinations

$$\begin{aligned}\mathcal{S}_a&=\mathcal{R}_a\cos\gamma+\mathcal{R}_b\sin\gamma\\ \mathcal{S}_b&=\mathcal{R}_a\sin\gamma-\mathcal{R}_b\cos\gamma\end{aligned} \tag{6}$$

have vectors which will point in a fixed direction relative to the framework. Consequently in terms of these coordinates the dot products of the vectors (and therefore the kinetic energy) are independent of γ.

It is now necessary to consider the potential energy. In terms of valence-type coordinates it is reasonable that the force constants entirely inside the framework or entirely inside a top should be independent of γ. The only coordinates connecting a top to the framework are of the type shown in Fig. 1. The force constants for the terms $(\Delta l_m)^2$, $(\Delta\alpha_A)^2$, $(\Delta\alpha_1)^2$, $(\Delta\alpha_A\Delta l_m)$ and $(\Delta\alpha_1\Delta l_m)$ may clearly be regarded as constant to a good approximation. However, force constants for such terms as $(\Delta\alpha_A\Delta\alpha_1)$ and other cross terms between coordinates in different parts of the molecule are very likely to depend on γ. Although many of these constants cannot be neglected, they are not large and as an approximation their average value may be used. This restriction

[6] Reference 5. Actually $2T=\Sigma G_{jj'}p_jp_{j'}$ where p_j is the momentum conjugate to R_j.

[7] In certain cases, e.g., if the top has symmetry C_{4v}, certain R's will have zero vectors associated with them at atom $m0$. These should be classed with those parallel to the top axis.

is not, however, necessary, as will be discussed below.

If average values are taken, then the potential energy in terms of R's will be independent of γ. Moreover, the transformations to $\mathcal{R}$'s and $\mathcal{S}$'s do not spoil the constancy of $2V$, because of the symmetry of the top. The degenerate coordinates $\mathcal{R}_a$ and $\mathcal{R}_b$ will always occur in pairs of terms with the same force constant; furthermore there will be no cross terms between degenerate and nondegenerate terms because of the symmetry of the top. All terms involving $\mathcal{R}_a$ will thus be of the form $(\mathcal{R}_a\mathcal{R}_{a'}+\mathcal{R}_b\mathcal{R}_{b'})$ which goes over into $(\mathcal{S}_a\mathcal{S}_{a'}+\mathcal{S}_b\mathcal{S}_{b'})$ on transformation by (6).

If the interaction constants such as that for $(\Delta\alpha_A\Delta\alpha_1)$, previously discussed, are allowed to vary with γ, it is required that the force constants in terms of the $\mathcal{S}$'s do not depend on γ, in order that the potential energy be of the form (5) and therefore the vibration frequencies be constant. This defines the γ dependence of the constants for $(\Delta\alpha_A\Delta\alpha_1)$, etc., but is a less stringent requirement than that they be invariant.

We have therefore shown that with certain restrictions on the interaction terms in the potential energy, the vibration frequencies will be independent of γ, since it is possible to find a set of coordinates in terms of which both the kinetic and potential energies of vibration are independent of γ. Accordingly, the normal coordinates will be linear combinations of these coordinates, the transformation having constant coefficients. It should be noted that while we have given the argument in terms of a valence-type potential energy (which we believe to be the best and most reasonable type), exactly similar restrictions would apply to a potential energy of any type.

Symmetry and Factoring of the Secular Equation

When molecules having attached tops are treated in this manner, i.e., when constant vibrational frequencies are assumed and the necessary restrictions are made on the potential energy, these molecules may often be treated as if they possessed a higher symmetry than in the case where a perfectly general potential function is used. A secular equation can be factored in a given system of coordinates if the coordinates can be divided into sets such that there are no cross terms connecting different sets in either the kinetic or potential energy.

If the molecule has symmetry there will be certain symmetry operations which when applied to the molecule in an arbitrary configuration will bring it into a new configuration not *indistinguishable* from the old one, but with the same kinetic and potential energies.[8] These operations, which may be defined with respect to planes and axes of the framework, and easily determined by inspection, will form a group **C**; the normal coordinates will form an irreducible representation of **C**. Since the normal coordinates are linear combinations of the $\mathcal{S}$'s, the latter will form a (reducible) representation of **C**, and may be used as basis coordinates in the ordinary group-theory methods.[9] The transformation properties of the $\mathcal{S}$'s will be given by the transformation properties of the vectors associated with them (see the discussion above) and are thus easily determined.[10]

From another viewpoint we may discuss the factoring in the following way. If the valence-type coordinates for each top (and for the framework) are formed into linear combinations (the $\mathcal{R}$'s of the previous section) which reduce the point group *of that top*, the terms in the kinetic and potential energies involving only the coordinates of the given top will show no cross terms between combinations ("top symmetry coordinates") of different symmetry. If in addition there were no cross terms between coordinates of the different tops and of the framework, the secular equation would factor into as many factors as would be obtained if each part of the molecule were treated as a separate molecule having its own symmetry. In the combined molecule this is not quite true because of the coupling terms between the parts. These will cause certain of the factors of the separate parts to combine into larger factors for the whole molecule.

[8] For a discussion of this distinction, see J. B. Howard, J. Chem. Phys. **5**, 442 (1937).

[9] J. Rosenthal and G. M. Murphy, Rev. Mod. Phys. **8**, 317 (1936).

[10] The $\mathcal{S}$'s with zero vectors, which will occur if a top of symmetry C_{4v} should ever be treated, may have somewhat different transformation properties.

The factors which will combine are found as follows. First consider the kinetic energy. Each top coordinate of type $\mathcal{S}$ will have a vector at atom $m0$ or mA either zero, or directly along the axis, or perpendicular to it, as previously discussed. Top coordinates will have kinetic energy cross terms with framework coordinates if and only if the vectors for one or more framework coordinates show a nonzero dot product with the vector for the top coordinate. If there is coupling, the two factors involved must be combined into a larger factor.

The potential energy coupling terms connecting the top and framework also need to be considered but usually they do not connect any factors not already connected by the kinetic energy terms.

In actually setting up the secular equation it is convenient to set the tops at selected fixed orientations and then use the symmetry coordinates $\mathcal{R}$ instead of $\mathcal{S}$. The orientations are chosen so that the vectors for the $\mathcal{R}$'s point in the right directions to produce the factoring. This point is illustrated below by tetramethylmethane.

An example: nitromethane

The coordinates belonging to the CH_3 group include the C-H extensions, H-C-H angles, and N-C-H angles, one of these six angles being redundant. The NO_2 coordinates are the N-O extensions, C-N-O angles and C-NO_2 angle. The C-N extension belongs equally to both groups. On reducing the representation[9] of C_{3v} one gets $2A_1+3E$ for CH_3 (redundancy eliminated) and for C_{2v}(NO_2 group) $2A_1+2B_1+B_2$. The C-N stretch belongs to A_1 of both. The coordinates of symmetry A_1 in each will couple because they each have vectors along the axis, as well as potential energy coupling terms. The coordinates of symmetry E will occur in pairs with vectors mutually perpendicular and perpendicular to the top axis. One-half of these (3) will couple with the B_1 coordinates of the framework, whose vectors lie in the NO_2 plane perpendicular to the axis. The other three will couple with the B_2, out of plane, coordinate. The factors of the secular equation in this case are therefore of degree 5, 5 and 4. If treated as a rigid molecule the most favorable result would be 9 and 6, for the degree of the factors, and the factoring would depend on the position of the methyl group.

Another example: ethane

Ethane is a somewhat different example because either end could serve as the framework, or some different treatment, such as that used by Howard,[8] could be employed which puts both ends on an equal basis. The H-C-H, H-C-C and C-H coordinates of one end will have the symmetry structure $2A_1+3E$ of C_{3v}. The A_1 coordinates of each end and the C-C stretch will combine as will each half of the E coordinates of each end. Moreover, because of the equivalence of the two ends, each of these factors will split into two factors, one with plus, the other with minus combinations of coordinates from the two ends. The final result is that factors of order 3, 2, 3 and 3 are obtained. The C-C stretch is necessarily symmetrical with respect to interchange of methyl groups so that the A_1 factor splits into factors of order 3 and 2 as shown.

An example: tetramethylmethane

As usual each methyl group has coordinates of symmetry $2A_1+3E$ of C_{3v}. The framework has the symmetry T_d, however, so it is possible to combine the four C-C extensions and the six C-C-C angles (only five are independent) into combinations of symmetry A_1+E+2T_2 of T_d. The four methyl groups are equivalent and symmetrically located so that their symmetry coordinates can be further combined. The $2A_1$ coordinates of each transform under T_d like their vectors at the outer carbon atoms so that the 8 combinations have the symmetry $2A_1+2T_2$ of T_d. The $3E$ coordinates transform like their vectors (i.e., X and Y) so that the result obtained is $3E+3T_1+3T_2$ of T_d. The E class will combine with the E framework combination, producing a quartic factor. The T_1 coordinates give a cubic. The coordinates of symmetry A_1 will give a cubic factor, while the T_2 symmetry yields a seventh-degree factor.

In actually setting up the secular equation the tops should be rotated until the vectors for the degenerate coordinates $\mathcal{R}_a$ and $\mathcal{R}_b$ point in convenient symmetrical directions and then the appropriate linear combinations of these should be made so as to reduce the group T_d.

Selection Rules

The selection rules for the infra-red and Raman will depend upon the electric moment and polarizability, respectively. If these quantities are expanded in powers of the top and framework symmetry coordinates ($\mathfrak{R}$'s, not $\mathfrak{S}$'s) three types of terms may be expected, i.e.:

$$\begin{aligned}\mu&=\mu^{(F)}+\mu^{(T)}+\mu^{(C)},\\ \alpha&=\alpha^{(F)}+\alpha^{(T)}+\alpha^{(C)}.\end{aligned}\tag{7}$$

Here $\mu^{(F)}$ is that part of the electric moment expansion which depends only on framework coordinates, $\mu^{(T)}$ is that part dependent on top coordinates only while $\mu^{(C)}$ depends on both. Similar remarks apply to the polarizability terms α.

As an approximation we shall assume that $\mu^{(F)}$ and $\alpha^{(F)}$ are not functions of γ and that the components of $\mu^{(T)}$ and $\alpha^{(T)}$, when taken in the direction of the moving top axes are likewise independent of γ. Furthermore we shall assume that the coupling terms $\mu^{(C)}$ and $\alpha^{(C)}$ are independent of γ, an approximation which affects only higher order terms.

The top angles γ will thus enter μ and α only through the following expressions.

$$\left.\begin{aligned}\mu_x^{(T)}&=\mu_\xi^{(T)}\cos\gamma+\mu_\eta^{(T)}\sin\gamma\\ \mu_y^{(T)}&=-\mu_\xi^{(T)}\sin\gamma+\mu_\eta^{(T)}\cos\gamma\end{aligned}\right\}$$

$$\left.\begin{aligned}\alpha_{xz}^{(T)}&=\alpha_{\xi\zeta}^{(T)}\cos\gamma+\alpha_{\eta\zeta}^{(T)}\sin\gamma\\ \alpha_{yz}^{(T)}&=-\alpha_{\xi\zeta}^{(T)}\sin\gamma+\alpha_{\eta\zeta}^{(T)}\cos\gamma\end{aligned}\right\}\tag{8}$$

$$\left.\begin{aligned}\tfrac{1}{2}(\alpha_{xx}^{(T)}-\alpha_{yy}^{(T)})&=\tfrac{1}{2}(\alpha_{\xi\xi}^{(T)}-\alpha_{\eta\eta}^{(T)})\cos 2\gamma\\ &\quad+\alpha_{\xi\eta}^{(T)}\sin 2\gamma\\ \alpha_{xy}^{(T)}&=-\tfrac{1}{2}(\alpha_{\xi\xi}^{(T)}-\alpha_{\eta\eta}^{(T)})\sin 2\gamma\\ &\quad+\alpha_{\xi\eta}^{(T)}\cos 2\gamma\end{aligned}\right\}$$

in which ξ, η are the Cartesian directions perpendicular to the top axis in the moving system, while x, y are the corresponding directions fixed in the framework. Naturally these directions x, y may not coincide with the principal axes of the molecule, a fact which must be considered in making quantitative intensity calculations.

The potential and kinetic energies were separated by the use of the coordinates $\mathfrak{S}$ of Eq. (6), which are linear combinations, in part involving γ, of the top symmetry coordinates. The quantities μ_ξ, μ_η, $\alpha_{\xi\zeta}$, etc., are independent of γ only when expressed in terms of the top symmetry coordinates themselves (the $\mathfrak{R}$'s) and not the $\mathfrak{S}$'s.

The transitions not involving vibration are determined by the terms independent of the vibrational symmetry coordinates. Since such terms all have the symmetry A_1, in the top group, they do not include μ_ξ, μ_η, $\alpha_{\eta\zeta}$, $\alpha_{\eta\zeta}$, $(\alpha_{\xi\xi}-\alpha_{\eta\eta})$ or $\alpha_{\xi\eta}$ and are therefore independent of γ. It does not follow, however, that no transition can occur, not involving vibration, between states essentially corresponding to different amounts of internal rotation. This is a result of the fact that the wave function cannot be accurately written as a product of a function of the Eulerian angles of framework axes and a function of the top angles, because of the coupling of internal and over-all rotation.[1] In the limiting case of no coupling (Ω_m of reference 1b equal to unity), vibrationless transitions cannot occur.

The transitions which involve a change of one vibrational quantum number by one unit plus possible changes in the internal rotational quantum numbers will depend mainly on the terms linear in the vibrational coordinates. These can easily be expressed as functions of the $\mathfrak{S}$'s by the use of Eq. (6). When this is done it is found that the linear terms in $\mu_x^{(T)}$, $\mu_y^{(T)}$ and $\alpha_{xz}^{(T)}$, $\alpha_{yz}^{(T)}$ become independent of γ while the linear terms of the others have the form

$$\tfrac{1}{2}(\alpha_{xx}^{(T)}-\alpha_{yy}^{(T)})=\sum_j \tau_j(\mathfrak{S}_a^{(j)}\cos 3\gamma-\mathfrak{S}_b^{(j)}\sin 3\gamma),$$

$$\alpha_{xy}^{(T)}=\sum_j \tau_j(-\mathfrak{S}_a^{(j)}\sin 3\gamma-\mathfrak{S}_b^{(j)}\cos 3\gamma).$$

Consequently *Raman-active transitions with unit change in one vibrational quantum number and some change in the internal rotational quantum number can occur for those vibrations which involve $\mathfrak{S}_a$ and $\mathfrak{S}_b$ and for those internal rotational transitions for which the matrix elements of sin 3γ or cos 3γ do not vanish.* Transitions involving other types of vibration and a change in internal

rotation are not, however, entirely barred for reasons similar to those given in the previous paragraph.

The appearance of the fundamental vibration frequencies alone, and their rotational structure and polarization, will be governed by the usual rules. The vibrations whose coordinates make up a factor of the secular equation will appear in the infra-red as fundamentals if either $\mu_x^{(F)}$, $\mu_y^{(F)}$, $\mu_z^{(F)}$, $\mu_\xi^{(T)}$, $\mu_\eta^{(T)}$, or $\mu_\zeta^{(T)}$ falls in that symmetry, and a Raman line will appear if one of the components of $\alpha^{(T)}$ or $\alpha^{(F)}$ has the symmetry of the given normal coordinate.

Appendix I.

If there are M internal coordinates which do not appear in the potential energy; i.e., whose force constants vanish, then there will be 3N–6–M normal coordinates which do not involve the M internal coordinates, and there will be M modes of zero frequency.

Let the internal coordinates be R, R_1 . . . R_{3N-6}, of which R_{3N-6-M}, . . . , R_{3N-6} do not appear in the potential energy; i.e.,

$$2V = \sum_{j,\, j'=1}^{3N-6-M} F_{jj'} R_j R_{j'}.$$

Now introduce a set of coordinates J_n which are linear combinations of the R_j chosen so that they are orthogonal (i.e., express the kinetic energy without cross terms) and so that the first $3N–6–M$ of them do not involve the last M R_j. In other words,

$$J_1 = R_1,$$
$$J_2 = R_1 + gR_2$$
$$J_3 = R_1 + g'R_2 + g''R_3, \text{ etc.},$$

where the g's are orthogonalizing constants. These equations can be inverted to give

$$R_1 = J_1$$
$$R_2 = hJ_1 + h'J_2, \text{ etc.}$$

Consequently the potential energy does not involve the last M J_n and the kinetic energy has no cross terms in the J_n. The last M rows and columns of the secular equation written in terms of the J_n will therefore consist entirely of zeros, except for the kinetic energy terms $(-\lambda)$ on the principal diagonal. There are thus M zero roots as stated and the other roots will correspond to modes of vibration which involve only the first $3N–6–M$ J_n and therefore the first $3N–6–M$ R_j.

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Anomalous Dispersion and Dielectric Loss in Polar Polymers

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A theory of dielectric loss of polar polymers at high dilution in a nonpolar plasticizer is developed. The theory leads to a broad distribution in relaxation times, associated with the internal rotatory Brownian motion of the hydrocarbon chain. An approximate relation between the degree of polymerization, the frequency of maximum loss, and the viscosity coefficient of a polar plastic is obtained. The loss factor is calculated from the theoretical relaxation time distribution for a mono-disperse polymer and for a poly-disperse polymer with an exponential distribution in chain length. The theoretical loss factor is compared with the experimental loss factor of polyvinyl chloride plasticized with diphenyl. The agreement with experiment is semi-quantitative.

I

THE most successful theory of anomalous dispersion and dielectric loss in liquids containing polar molecules is that of Debye.[1] Under the influence of an alternating electric field, a system of polar molecules is supposed to diffuse by rotatory Brownian motion toward an equilibrium distribution in molecular orientation, corresponding to a resultant dielectric polarization. When, at sufficiently high frequency, the rotatory diffusion becomes too slow for the establishment of equilibrium with the applied field, the polarization acquires a component out of phase with the field. As a consequence, the displacement

[1] Debye, *Polar Molecules* (Chemical Catalog Company, 1929).

current acquires a conductance component in phase with the field, resulting in thermal dissipation of energy from the field. The dependence of the loss factor on frequency is determined by the relaxation time, which is the interval required for the polarization in a static field to diminish to a fraction $1/e$ of its equilibrium value when the field is suddenly removed. The Debye theory, originally developed for spherical molecules with rigid dipoles and a single relaxation time, has been extended to ellipsoidal molecules with three relaxation times.

Polar high polymers of the type $(CH_2CHX)_n$ exhibit anomalous dispersion and dielectric loss at frequencies many decades lower than do simple polar molecules.[2] However, their loss curves cannot be analyzed in terms of a single relaxation time or a small finite set of relaxation times, but instead correspond to a broad distribution in relaxation times.[3] From a qualitative point of view, this is not difficult to understand. The polymer chains possess many degrees of internal rotational freedom. These allow many varieties of internal Brownian motion in which segments of the chain diffuse from one relative configuration to another with changing dipole moment. To each such mode of internal rotatory diffusion, involving a coiling or uncoiling of the chain or a segment of the chain, there should correspond a characteristic relaxation time.

In the present article, we shall develop a theory of dielectric loss in solutions containing nonrigid polar molecules of many internal degrees of freedom. Finally, we shall discuss the application of the theory to polar polymers of the type $(CH_2CHX)_n$, represented by a somewhat simplified model. The general theory could, of course, be deduced from the quantum-mechanical theory of dispersion,[4] but the necessary asymptotic classical formulas are more easily obtained by following the lines of the theory of Debye. The validity of the theory in no way depends upon an assumed mechanism of the internal rotatory diffusion. However, in the applications, we shall find it convenient to calculate the internal diffusion tensor of a long chain molecule on the basis of a rough hydrodynamical model. Since it is to be applied to polymers highly diluted with a nonpolar plasticizer, we develop the theory for a dilute solution of polar molecules in a nonpolar solvent.

[2] Fuoss, J. Am. Chem. Soc. **61**, 2334 (1939).
[3] Fuoss and Kirkwood, J. Am. Chem. Soc. **63**, 385 (1941).
[4] Gorter and de L. Kronig, Physica **3**, 1009 (1936).

II

A binary mixture consisting of N_1 molecules of a nonpolar species and N_2 molecules of a polar species has an electric susceptibility

$$\frac{\epsilon-1}{4\pi}=\frac{1}{V}\{N_1\alpha_1+N_2(\alpha_2+p)\}\frac{F}{E}, \tag{1}$$

where V the volume of the specimen, F/E the ratio of the local field to the applied electric field, p the average electric moment induced by unit field in a molecule of the polar species as the result of dipole orientation, and α_1 and α_2 are the optical polarizabilities of the respective molecules. The best approximation to the local field is that of Onsager.[5,6] If local dipole-dipole interaction is neglected, the simple Onsager local field is equal to $[3\epsilon/(2\epsilon+1)]E$, with a slightly modified factor for nonspherical molecules. Using this local field we may write

$$\left[\frac{(\epsilon-1)(2\epsilon+1)}{9\epsilon}-\frac{(n_0^2-1)(2n_0^2+1)}{9n_0^2}\right]\frac{v}{x_2}=P$$
$$P=\frac{4\pi N}{3}p, \quad v=(M_1x_1+M_2x_2)/\rho, \tag{2}$$

where n_0 is the optical refractive index of the solution extrapolated to infinite wave-length, v is the mean molal volume, ρ the density, M_1 and M_2 the molecular weights, and x_1 and x_2 the mole fractions of the respective species. In the treatment of high polymers, it is somewhat more convenient to define P as the polarization per monomer unit

$$P=\frac{4\pi N}{3}\frac{p}{n}, \tag{3}$$

where n is the degree of polymerization. With this convention Eqs. (2) remain valid if M_2 is the molecular weight of the monomer, and x_2 is computed as the mole fraction on a monomer

[5] Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).
[6] Kirkwood, J. Chem. Phys. **7**, 911 (1939).

basis. If the applied electric field is an alternating field $Ee^{i\omega t}$ of frequency $\omega/2\pi$, both ϵ and P are complex quantities,

$$\begin{aligned}\epsilon&=\epsilon'-i\epsilon''\\ P&=P'-iP'',\end{aligned} \tag{4}$$

where ϵ' is the real dielectric constant and ϵ'' the loss factor. For convenience in theoretical discussion, it is convenient to define a reduced polarization $Q(\omega)$ as follows,

$$\begin{aligned}Q(\omega)&=P(\omega)/P_0\\ &=J(\omega)-iH(\omega),\end{aligned} \tag{5}$$

where P_0 is the polarization at zero frequency.

We suppose a molecule of the polar species to possess r internal degrees of freedom. When acted upon by the local field $Fe^{i\omega t}$, its electric moment acquires a nonvanishing component in the direction of the field. The vector moment $\mathbf{\mu}(q_1, \cdots q_r)$ of the molecule must depend upon the coordinates $q_1, \cdots q_r$ specifying its internal configuration. Its mean component $(\mathbf{\mu}\cdot\mathbf{e}_1)_{Av}$ in the direction $\mathbf{e}_1$ of the applied field is

$$(\mathbf{\mu}\cdot\mathbf{e}_1)_{Av}=\int \mathbf{e}_1\cdot\mathbf{\mu}(q)f(q,t)dq, \tag{6}$$

where $f(q, t)$ is the molecular probability distribution function in the internal configuration space $q_1, \cdots q_r$, and dq denotes a volume element in that space. If the amplitude of the applied field is small we may employ the expansions,

$$\begin{aligned}f&=f_0[1+f_1Fe^{i\omega t}+O(F^2)],\\ (\mathbf{\mu}\cdot\mathbf{e}_1)_{Av}&=pFe^{i\omega t}+O(F^2),\end{aligned} \tag{7}$$

where f_0 is the distribution function appropriate to equilibrium in the absence of the field. Since the mean moment in any direction vanishes in the absence of the applied field, we obtain from Eqs. (6) and (7)

$$p=\int \mathbf{e}_1\cdot\mathbf{\mu}(q)f_0(q)f_1(q)dq. \tag{8}$$

In order to determine the distribution function $f(q, t)$, it is necessary to investigate the configurational diffusion of a molecule by Brownian motion under the influence of an external force. The distribution function satisfies the diffusion equation,

$$\nabla\cdot\mathbf{D}\cdot\{\nabla f+f\nabla V/kT\}=\partial f/\partial t, \tag{9}$$

where $\mathbf{D}$ is the internal diffusion tensor expressed in dyadic form, ∇ the gradient operator in the r dimensional configuration space, and V the potential of internal and external forces. By the Einstein theory of Brownian motion, the diffusion tensor $\mathbf{D}$ is related to the mobility tensor $\mathbf{u}$ as follows

$$\mathbf{D}=\mathbf{u}kT, \tag{10}$$

where k is Boltzmann's constant and T the Kelvin temperature. At equilibrium, in the absence of external forces, the solution of Eq. (6) is

$$f_0=A_0e^{-V_0/kT},\quad A_0^{-1}=\int e^{-V_0/kT}dq, \tag{11}$$

where V_0 is the potential of internal forces alone. Thus the expansion, Eq. (7), becomes

$$f=A_0e^{-V_0/kT}[1+f_1(q)Fe^{i\omega t}+O(F^2)]. \tag{12}$$

In an applied electric field $Fe^{i\omega t}$, the potential energy becomes

$$V=V_0-\mathbf{\mu}\cdot Fe^{i\omega t}. \tag{13}$$

Substitution of (12) and (13) in Eq. (9), yields

$$\begin{aligned}&L(f_1-\mathbf{\mu}\cdot\mathbf{e}_1/kT)-i\omega f_1=0,\\ &\omega\to 0;\quad f_1\to(\mathbf{\mu}\cdot\mathbf{e}_1)/kT,\\ &L=e^{V_0/kT}\nabla\cdot(e^{-V_0/kT}\mathbf{D}\cdot\nabla).\end{aligned} \tag{14}$$

In order to solve Eq. (14), we consider the operator

$$\begin{aligned}&L_0=\nabla\cdot\mathbf{D}\cdot\nabla+U(q),\\ &U=\frac{1}{2kT}(\nabla\cdot\mathbf{D}\cdot\nabla)V_0-\frac{1}{(2kT)^2}(\nabla V_0)\cdot\mathbf{D}\cdot(\nabla V_0).\end{aligned} \tag{15}$$

Let us suppose that L_0 is self-adjoint, and consider the eigenvalue problem,

$$L_0\psi+\lambda\psi=0, \tag{16}$$

subject to the conditions that ψ be continuous, single valued and quadratically integrable in the space $q_1, \cdots q_r$. L_0 will possess a set of eigenvalues, $-\lambda$, and eigenfunctions ψ_λ forming a complete orthogonal set. It may be verified by substitution that

$$L(e^{V_0/2kT}\psi_\lambda)+\lambda\psi_\lambda e^{V_0/2kT}=0. \tag{17}$$

We proceed to expand $f_1e^{-V_0/2kT}$ and $(\mathbf{\mu}\cdot\mathbf{e}_1)e^{-V_0/2kT}$

in the orthogonal set ψ_λ, assumed normalized,

$$f_1 e^{-V_0/2kT} = \sum_\lambda B_\lambda \psi_\lambda,$$
$$(\boldsymbol{\mu}\cdot\mathbf{e}_1) e^{-V_0/2kT} = \frac{1}{(3A_0)^{\frac{1}{2}}} \sum_\lambda \mu_\lambda \psi_\lambda. \tag{18}$$
$$\mu_\lambda = (3A_0)^{\frac{1}{2}} \int (\boldsymbol{\mu}\cdot\mathbf{e}_1) e^{-V_0/2kT} \psi_\lambda^* dq.$$

Substitution of the expansions (18) in Eq. (14) with use of (16) and the orthogonality property of the ψ_λ, yields the desired solution

$$B_\lambda = \frac{1}{(3A_0)^{\frac{1}{2}}} \frac{\mu_\lambda}{1+i\omega\tau_\lambda}, \quad \tau_\lambda = 1/\lambda,$$
$$f_1 = \frac{1}{(3A_0)^{\frac{1}{2}} kT} \sum_\lambda \frac{\mu_\lambda \psi_\lambda e^{V_0/2kT}}{1+i\omega\tau_\lambda}. \tag{19}$$

Substitution in the integral (8) of the expansions (18) and (19) for $(\boldsymbol{\mu}\cdot\mathbf{e}_1)$ and f_1 and the expression for f_0, Eq. (11), yields

$$p = \frac{1}{3kT} \sum_\lambda \frac{|\mu_\lambda|^2}{1+i\omega\tau_\lambda}. \tag{20}$$

At zero frequency of the applied field, we have

$$p_0 = \frac{1}{3kT} \overline{\mu_2},$$
$$\overline{\mu_2} = 3A_0 \int (\boldsymbol{\mu}\cdot\mathbf{e}_1)^2 e^{-V_0/kT} dq = A_0 \int \mu^2 e^{-V_0/kT} dq', \tag{21}$$

where dq' represents a volume element of the internal configuration space exclusive of the coordinates specifying the orientation of the molecule as a whole relative to an external reference system. Thus $\overline{\mu^2}$ is the mean square moment of the molecule averaged over its internal coordinates. From Eq. (3), we know that P/P_0 is identical with p/p_0, so that we may write, $P/P_0 = Q$,

$$Q(\omega) = \sum_\lambda \frac{Q(\lambda)}{1+i\omega\tau_\lambda},$$
$$Q_\lambda = |\mu_\lambda|^2/\overline{\mu^2}. \tag{22}$$

If the eigenvalues λ are closely spaced, we may smooth to a continuum and approximate the sum in Eq. (21) by an integral

$$Q(\omega) = \int_0^\infty \frac{G(\tau)}{1+i\omega\tau} d\tau,$$
$$G(\tau) = Q(1/\tau)\rho(1/\tau)/\tau^2, \tag{23}$$

where $\rho(\lambda)$ is density of eigenvalues λ. This may be computed as follows:

$$Q(\lambda)\rho(\lambda) = d\Omega/d\lambda,$$
$$\Omega(\lambda) = \sum_{\lambda'<\lambda} Q(\lambda'), \tag{24}$$

where the sum defining $\Omega(\lambda)$ extends over all eigenvalues λ' which are less than λ.

III

We shall now discuss the application of the theory to a linear polymer molecule $(CH_2-CHX)_n$ in which X is a monatomic dipolar substituent. We denote the directions of the successive C−C bonds of the polymer skeleton by unit vectors $\mathbf{a}_2, \cdots \mathbf{a}_{2n}$, and the directions of the C−X bonds branching from the skeleton by $\mathbf{b}_2, \mathbf{b}_4, \cdots \mathbf{b}_{2n}$. The configuration of the chain is conveniently specified by the $2n+1$ coordinates $\vartheta, \varphi, \varphi_1, \varphi_2, \cdots \varphi_{2n-1}$. The angles ϑ and φ specify the orientation of bond $\mathbf{a}_{n+1}$ relative to a fixed coordinate system $\mathbf{i}, \mathbf{j}, \mathbf{k}$ with $\mathbf{k}$ as polar axis; φ_{n+1} is the angle between the planes $(\mathbf{a}_{n+2}, \mathbf{a}_{n+1})$ and $(\mathbf{a}_{n+1}, \mathbf{k})$; φ_n the angle between the planes $(\mathbf{a}_n, \mathbf{a}_{n+1})$ and $(\mathbf{a}_{n+1}, \mathbf{k})$; φ_l the angle between planes $(\mathbf{a}_{l+1}, \mathbf{a}_l)$ and $\mathbf{a}_l, \mathbf{a}_{l-1}$ if $l > n+1$ or between the planes $(\mathbf{a}_{l+2}, \mathbf{a}_{l+1})$ and $(\mathbf{a}_{l+1}, \mathbf{a}_l)$, if $l < n$. If $\mathbf{k}$ is chosen parallel to $\mathbf{e}_1$, the direction of the applied electric field, we may write

$$(\boldsymbol{\mu}\cdot\mathbf{e}_1) = \mu_X \sum_{l=2,4}^{2n} \beta^{(l)},$$
$$\beta^{(l)} = \mathbf{k}\cdot\mathbf{b}_l, \tag{25}$$

where μ_X is the scalar dipole moment of the C−X bond. In order to express the cosines $\beta^{(l)}$ as functions of the coordinates $\vartheta, \varphi, \varphi_1, \cdots \varphi_{2n-1}$, we consider the linear transformation $\mathbf{\Lambda}(\vartheta, \varphi)$ with the matrix,

$$\begin{pmatrix} \cos\vartheta\cos\varphi & -\sin\varphi & \sin\vartheta\cos\varphi \\ \cos\vartheta\sin\varphi & \cos\varphi & \sin\vartheta\sin\varphi \\ -\sin\vartheta & 0 & \cos\vartheta \end{pmatrix}.$$

For purposes of computation it is convenient to express $\mathbf{\Lambda}$ in dyadic form,

$$\begin{aligned}
&\mathbf{\Lambda}(\vartheta, \varphi)=\mathbf{\Lambda}_0+\mathbf{\Lambda}_+e^{i\varphi}+\mathbf{\Lambda}_-e^{-i\varphi},\\
&\mathbf{\Lambda}_0=\cos\vartheta\mathbf{k}\cdot\mathbf{k}-\sin\vartheta\mathbf{ki},\\
&\mathbf{\Lambda}_+=\tfrac{1}{2}\{[\mathbf{jj}-\mathbf{ij}]+\cos\vartheta[\mathbf{ii}+\mathbf{ji}]\\
&\qquad\qquad +\sin\vartheta[\mathbf{ik}+\mathbf{jk}]\},\\
&\mathbf{\Lambda}_-=\tfrac{1}{2}\{[\mathbf{jj}-\mathbf{ij}]+\cos\vartheta[\mathbf{ii}-\mathbf{ji}]\\
&\qquad\qquad +\sin\vartheta[\mathbf{ik}-\mathbf{jk}]\}.
\end{aligned}\tag{26}$$

The vectors $\mathbf{a}_l$ may be obtained from the fixed vector $\mathbf{k}$ by the following transformation

$$\begin{aligned}
&\mathbf{a}_{n+1}=\mathbf{\Lambda}(\vartheta, \varphi)\cdot\mathbf{k},\\
&\mathbf{a}_l=\prod_{s=l-1}^{n+1}\mathbf{\Lambda}(\gamma, \varphi_s)\mathbf{a}_{n+1}, \quad l>n+1\\
&\mathbf{a}_l=\prod_{s=l+1}^{n}\mathbf{\Lambda}(\gamma, \varphi_s)\mathbf{a}_{n+1}, \quad l<n\\
&\mathbf{b}_l=\mathbf{\Lambda}(\gamma, \varphi_l+\pi/3)\cdot\mathbf{a}_l, \quad l>n+1\\
&\quad=-\mathbf{\Lambda}(\gamma, \varphi_l+\pi/3)\cdot\mathbf{a}_{l+1}, \quad l<n,
\end{aligned}\tag{27}$$

where γ is the supplement of the skeletal bond angle. Equations (26) and (27) lead to the following expressions for the $\beta^{(l)}$:

$$\begin{aligned}
\beta^{(l)}&=\mathbf{k}\cdot\mathbf{\Lambda}_0(\gamma)\prod_{s=l-1}^{n+1}\mathbf{\Lambda}(\gamma, \varphi_s)\mathbf{\Lambda}(\vartheta, \varphi)\cdot\mathbf{k};\\
&\qquad\qquad l>(n+1)\\
&=-\mathbf{k}\cdot\mathbf{\Lambda}_0(\gamma)\prod_{s=l+2}^{n}\mathbf{\Lambda}(\gamma, \varphi_s)\mathbf{\Lambda}(\vartheta, \varphi)\cdot\mathbf{k};\\
&\qquad\qquad l<n.
\end{aligned}\tag{28}$$

The determination of the relaxation time distribution now depends upon the calculation of the coefficients μ_λ,

$$\begin{aligned}
&\mu_\lambda=\mu_X\sum_{l=2,4}^{2n}\beta_\lambda{}^{(l)},\\
&\beta_\lambda{}^{(l)}=(3A_0)^{\frac{1}{2}}\int_0^{\pi}\int_0^{2\pi}\cdots\int_0^{2\pi}e^{-V_0/2kT}\\
&\qquad\qquad\times\beta^{(l)}\psi_\lambda{}^*\sin\vartheta d\vartheta d\varphi\cdots d\varphi_{2m+1},
\end{aligned}\tag{29}$$

where the ψ_λ are the eigenfunctions of the operator L_0, Eq. (16), appropriate to the internal rotatory diffusion of the chain $(CH_2CHX)_n$, immersed in a viscous fluid, with intramolecular hindering torques having a potential V_0.

The determination of the internal rotatory diffusion tensor for a polymer chain immersed in a viscous fluid is an almost prohibitively difficult hydrodynamical problem. However, the resistance tensor, $\mathbf{u}^{-1}$ may be roughly estimated by treating the individual monomer units as spheres of equivalent volume without hydrodynamical interaction (see Appendix I). The resistance tensor so obtained is not diagonal for the coordinates ϑ, φ, φ_1, $\cdots\varphi_{2n-1}$ which we have employed, but becomes so, when averaged over all configurations of the chain with center of gravity fixed at the midpoint of the bond $\mathbf{a}_{n+1}$. If we approximate the skeletal bond angle by $\pi/2$, and define a mean diffusion tensor as $kT[(\mathbf{u}^{-1})_{Av}]^{-1}$, we obtain a diagonal tensor with elements,

$$\begin{aligned}
&\bar{D}_{\vartheta\vartheta}=\bar{D}_{\varphi\varphi}=2D_0,\\
&\bar{D}_{ss}=\frac{D_0}{(1-|s-n|/n)^2}, \quad s=1, \cdots 2n-1\\
&D_0=\frac{kT}{2\pi n^2\eta}a^2b,\\
&b=(3\Delta/8\pi)^{\frac{1}{2}},
\end{aligned}\tag{30}$$

where Δ is the volume of a monomer unit, a the C−C distance, and η is the viscosity coefficient of the fluid in which the molecule is immersed. The diffusion constants $D_{\vartheta\vartheta}$ and $D_{\varphi\varphi}$ for rotation of the chain as a whole are inversely proportional to the square of the chain length, hence very small for high polymers. The diffusion constants for internal rotation around a specified bond are small in the middle of the chain, but become large in the vicinity of the ends. It is, of course, to be emphasized that only the qualitative features and the order of magnitude of $\bar{D}$ are significant. Under the influence of an applied electric field of small intensity, it is not to be expected that the molecule will diffuse far from its equilibrium configuration. We may therefore hope to obtain reasonable results by approximating the actual diffusion tensor by $\bar{D}$. We shall further assume that the internal hindering torques have a potential V_0 for which $\partial V_0/\partial\varphi_s$ vanishes for every s. Although this is not actually the case in real hydrocarbon chains, hindered rotation may be simulated by a step-function potential with an appropriate number of minima, for which

$\partial V_0/\partial\varphi_s$ vanishes except on a finite set of points. If, in addition, the skeletal bond angle is approximated by $\pi/2$, the operator L_0, Eq. (15) becomes

$$L_0=D_0\left\{2\left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right)+\frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right]+\sum_{s=1}^{2n-1}g(|s-n|)\frac{\partial^2}{\partial\varphi_s{}^2}\right\}, \tag{31}$$

$$g(|s-n|)=[1-|s-n|/n]^{-2}.$$

The eigenfunctions and eigenvalues of L_0 are

$$\lambda=D_0[2K(K+1)+\sum_{s=1}^{2n-1}m_s{}^2g(|n-s|)], \tag{32}$$

$$\psi_\lambda=[((2K+1)/2)(K-|m|)!/(K+|m|)!]^{\frac{1}{2}}(2\pi)^{-(2m+1)/2}P_K{}^m(\cos\theta)e^{im\varphi}\prod_{s=1}^{2n-1}e^{im_s\varphi_s}.$$

For the present we shall neglect internal hindering torques. With $V_0=0$, the calculation of the coefficients $\beta_\lambda{}^{(l)}$, Eq. (29), leads to the result (see Appendix II)

$$\begin{aligned}
|\beta_\lambda{}^{(l)}| &= 2^{-\sigma}(\prod_{s=1}^{n}\delta_{m_s,0})(\prod_{s=l}^{2n-1}\delta_{m_s,0})\,Y(m_{n+1},m)\,;\quad l>n+1\\
&= 2^{-\sigma}(\prod_{s=1}^{l+1}\delta_{m_s,0})(\prod_{s=n+1}^{2n-1}\delta_{m_s,0})\,Y(m_n,m)\,;\quad l<n,\\
\beta_\lambda{}^{(l)}&=0\begin{cases}K\neq 1\\ m_s>1 \text{ any } s\\ m_{s+1}=m_s=0 \text{ any } s \text{ in } \begin{cases}n+1\leqslant s\leqslant l-1\\ l+2\leqslant s\leqslant n,\end{cases}\end{cases}\\
\sigma&=\sum_{s=1}^{2n-1}m_s{}^2,
\end{aligned} \tag{33}$$

$$Y(m',m)=\delta_{m',0}(\delta_{m,1}+\delta_{m,-1})/\sqrt{2}+\delta_{m',1}[\delta_{m,0}+(\delta_{m,1}+\delta_{m,-1})/\sqrt{2}]+\delta_{m',-1}[\delta_{m,0}+(\delta_{m,1}+\delta_{m,-1})/\sqrt{2}],$$

where δ is the Kroneker delta function. Due to the delta function products and the fact that neighboring m_s cannot be simultaneously zero, all products $\beta_\lambda{}^{(l)}\beta_\lambda{}^{(l')}$ vanish if $l\neq l'$ and we may write,

$$|\mu_\lambda|^2=\mu_X{}^2\sum_{l=2}^{2n}|\beta_\lambda{}^{(l)}|^2. \tag{34}$$

In preparation for the calculation of $Q(\lambda)$, we proceed to calculate a sum $\omega(L,\sigma)$ defined as follows,

$$\omega(L,\sigma)=\sum_{\substack{\lambda\\ \Sigma m_s{}^2=\sigma}}|\beta_\lambda{}^{(l)}|^2,\quad L=|l-n|, \tag{35}$$

where the sum extends over all eigenvalues consistent with a specified value σ of the sum $\sum m_s{}^2$. It turns out that this sum depends only on the absolute value L of $|l-n|$. Utilizing the fact that there are 2^σ ways of distributing the values ±1 among the m_s in a specified arrangement and the fact that $\beta_\lambda{}^{(l)}$ vanishes if the product $\Lambda_0{}^2$ occurs, we calculate from Eq. (33),

$$\omega(L,\sigma)=2^{-\sigma}\{2C(L,\sigma)+C_0(L,\sigma)\}, \tag{36}$$

where $C(L,\sigma)$ is the number of ways $|l-n|$ sites may be distributed among $|l-n|-\sigma$ elements $\mathbf{\Lambda}_0$ with no nearest neighbor contacts and with one terminal element $\mathbf{\Lambda}_0$; $C_0(L,\sigma)$ the number of ways of

distribution with both terminal sites occupied by Λ_0. Using Ising's[7] result for these numbers, we have

$$\omega(L,\sigma)=2^{-(\sigma-1)}\binom{\sigma-1}{L-\sigma-1}+2^{-\sigma}\binom{\sigma-1}{L-\sigma-2}. \tag{37}$$

Since we are concerned with molecules of many internal degrees of freedom, it will be sufficient for our purposes to obtain formulas asymptotically valid for large σ and L. When σ is large, we may use the Gaussian approximation to the binomial coefficients and write per unit L interval

$$\begin{aligned}\omega(L,\sigma)&=3(2/\pi\sigma)^{\frac{1}{2}}e^{-2[L-3\sigma/2]^2/\sigma};\quad \sigma\leqslant L\leqslant 2\sigma\\ &=0;\quad L>2\sigma \text{ or } L<\sigma.\end{aligned} \tag{38}$$

We shall also need a sum $\nu(L,\sigma)$, over even values of l,

$$\sum_{L'=1}^{L}\omega(L',\sigma),$$

which may be calculated with the aid of Eq. (38) and approximation of the sum by an integral,

$$\begin{aligned}\nu(L,\sigma)&=\sum_{L'=1}^{L}\omega(L',\sigma)=\frac{3}{4}\left[1+\text{sign}\left(L-\frac{3\sigma}{2}\right)\right]+O(e^{-(9\sigma/8)(2L-1/3\sigma)^2}),\\ &=\tfrac{3}{2},\quad 1\leqslant\sigma<2L/3\\ &=0,\quad \sigma>2L/3.\end{aligned} \tag{39}$$

With Eqs. (34), (35), and (39) at our disposal, we are able to calculate $\overline{\mu^2}$, equal to $\sum_\lambda|\mu_\lambda|^2$,

$$\overline{\mu^2}=\mu_X{}^2\sum_{\sigma=1}^{2n-1}\nu(n-1,\sigma)=n\mu_X{}^2, \tag{40}$$

since the sum over even values of l in the interval, $2\leqslant l\leqslant 2n$, of a summand depending only on $|l-n|$, may be adequately approximated by an integral over L in the interval $1\leqslant L\leqslant n-1$. The result (40) may be obtained in a more direct manner, and it serves as a check on the calculation of the $\beta_\lambda{}^{(l)}$.

By Eqs. (34) and (40), we may write for $\Omega(\lambda)$, Eq. (24), from which the relaxation time distribution function is to be computed,

$$\Omega(\lambda)=\frac{1}{n}\sum_{l=2}^{2n}\sum_{\lambda'<\lambda}|\beta_{\lambda'}{}^{(l)}|^2, \tag{41}$$

where the sum over λ' extends over all eigenvalues less than λ. We may also write

$$\begin{aligned}\Omega(\lambda)&=\frac{1}{n}\sum_{\sigma=1}^{2n-1}\sum_{l=2}^{2n}\omega(L,\sigma,\lambda),\\ \omega(L,\sigma,\lambda)&=\sum_{\substack{\lambda'<\lambda\\ \Sigma m_s{}^2=\sigma}}|\beta_{\lambda'}{}^{(l)}|^2,\end{aligned} \tag{42}$$

where the functions $\omega(L,\sigma,\lambda)$ differ from the $\omega(L,\sigma)$ in that the sums defining them extend only over the set of eigenvalues $\lambda'<\lambda$, instead of over all eigenvalues. The set of eigenvalues, Eq. (32), on which a given $\beta_\lambda{}^{(l)}$ is nonvanishing are defined by

$$\begin{aligned}\lambda&=D_0[4+\sum_{s=1}^{L-1}m_s{}^2g(s)],\\ g(s)&=\frac{1}{(1-s/n)^2}.\end{aligned} \tag{43}$$

The average value of $\overline{m_s{}^2}$, consistent with a specified σ, over all distributions of the $|l-n|$ sites among $m_s{}^2$ values of 0 and 1 with no contacts between elements Λ_0 corresponding to $m_s{}^2=0$, is σ/L. Thus the average eigenvalue for a specified σ and L is

$$\bar{\lambda}(L,\sigma)=D_0\left\{4+\frac{\sigma}{L}\sum_{s=1}^{L-1}g(s)\right\}. \tag{44}$$

If the sum in Eq. (44) is approximated by an integral, we have

$$\bar{\lambda}(L,\sigma)=D_0\left\{4+\frac{\sigma}{1-L/n}\right\}+O\left(\frac{1}{L(1-L/n)}\right), \tag{45}$$

[7] Ising, Zeits. f. Physik **31**, 253 (1925).

which is an adequate approximation except for very small L and very large L in the immediate neighborhood of n. Since the fluctuation $\overline{(\lambda-\bar{\lambda})^2}/\bar{\lambda}^2$ is of the order of $1/\sigma$, we may say, for large σ.

$$\begin{aligned}\omega(L,\sigma,\lambda)&=\omega(L,\sigma), \quad \lambda<\bar{\lambda}(L,\sigma),\\ &=0, \quad \lambda>\bar{\lambda}(L,\sigma).\end{aligned} \tag{46}$$

Since $\bar{\lambda}(L,\sigma)$ is a monotone increasing function of L, we may write

$$\begin{aligned}\omega(L,\sigma,\lambda)&=\omega(L,\sigma), \quad 1\leqslant L\leqslant L_0,\\ &=0, \quad L>L_0,\end{aligned} \tag{47}$$

where L_0 is the positive real solution of the equation

$$\begin{aligned}&\bar{\lambda}(L_0,\sigma)=\lambda,\\ &L_0(\lambda,\sigma)=n(1-\sigma D_0/\lambda).\end{aligned} \tag{48}$$

From Eqs. (39), (42), and (47), we have

$$\Omega(\lambda)=\frac{1}{n}\sum_{s=1}^{2n-1}\nu(L_0,\sigma)=\frac{3}{2n}\sigma_\lambda, \tag{49}$$

where σ_λ satisfies the equation,

$$\begin{aligned}&\sigma_\lambda=\frac{2}{3}L_0=\frac{2n}{3}\left(1-\frac{\sigma_\lambda D_0}{\lambda}\right),\\ &\sigma_\lambda=\frac{2n}{3}\left(1+\frac{2nD_0}{3\lambda}\right)^{-1}.\end{aligned} \tag{50}$$

And we finally obtain the asymptotic result,

$$\begin{aligned}&\Omega(\lambda)=\lambda\tau_0/(1+\lambda\tau_0), \quad \tau_0=3/2nD_0;\\ &6/n\tau_0\leqslant\lambda\leqslant n\pi^2/4\tau_0.\end{aligned} \tag{51}$$

This formula ceases to be valid at either end of the λ interval, but is an adequate approximation in the interior. Use of Eqs. (23), (24) and (51) leads to the desired relaxation time distribution function,

$$\begin{aligned}G(\tau)&=\frac{\tau_0}{(\tau+\tau_0)^2}; \quad \frac{4\tau_0}{n\pi^2}\leqslant\tau\leqslant\frac{n\tau}{6}\\ &=0, \quad \tau>\frac{n\tau_0}{6} \text{ or } \tau<\frac{4\tau_0}{n\pi^2}.\end{aligned} \tag{52}$$

It is easily verified that except for terms $0(1/n)$, $G(\tau)$ is normalized,

$$\int_0^\infty G(\tau)d\tau=1.$$

We remark that since n^2D_0 is of the order of magnitude of the rotatory diffusion constant of a single monomer unit, τ_0 is of the order of n times the relaxation time of a single monomer unit.

The evaluation of the real and imaginary parts, J and $-H$, of the function $Q(\omega)$, Eq. (23), with the aid of the distribution function $G(\tau)$ of Eq. (52) leads to the result,

$$\begin{aligned}J(x)&=\frac{1}{(1+x^2)^2}\left\{(1+x^2)+\frac{\pi x}{2}(x^2-1)-2x^2\log x\right\},\\ H(x)&=\frac{x}{(1+x^2)^2}\{(x^2-1)\log x-x^2+\pi x-1\},\\ x&=\omega\tau_0.\end{aligned} \tag{53}$$

The function $H(x)$ reaches a maximum value H_m of 0.286 at $x=1$. At this frequency $1/\tau_0$, $J(x)$ has the value 0.500. On the Debye theory with a single relaxation time, H_m has the value 0.500. Thus the broad distribution in relaxation time, exhibited by a polymer, according to Eq. (52), broadens and lowers the loss factor-frequency curve, though not to the extent one might expect on qualitative grounds. The frequency of maximum loss ω_m, equal to $1/\tau_0$ is related to the structure of the polymer in the following way, according to Eqs. (30) and (51),

$$\omega_m=\frac{1}{n\tau^*}, \quad \tau^*=3\pi a^2b\eta/kT, \tag{54}$$

where τ^* is a relaxation time of a magnitude appropriate to a single monomer unit. Thus from the frequency of maximum loss, it should be possible to estimate the degree of polymerization n as $(\omega_m\tau^*)^{-1}$, in terms of the coefficient of viscosity η of the medium and the volume of a monomer unit. Such an estimate would necessarily be rough, of logarithmic accuracy, because of the approximations made in the estimation of the diffusion tensor.

The foregoing calculations are appropriate to a monodisperse linear polymer with no branching. In unfractionated polymer specimens, there is actually a distribution in the degree of polymerization n and a certain degree of branching of the chains. Thus, while the theory agrees roughly with experiment, the observed value of H_m for polyvinyl chloride is considerably lower than the

value 0.29 predicted by the theory. It therefore seems necessary to elaborate the theory to take into account the polydisperse character of most polymer systems, as well as the possible branching of the chain. We shall not undertake an analysis of the effect of branching, but we shall examine the effect of a distribution in chain length. If we define P_0 as $4\pi N\bar{n}\mu_X^2/9kT$ and $\bar{Q}(\omega)$ as the ratio $P/\bar{P}_0$, with $\bar{n}$ the average degree of polymerization, and treat the polydisperse system as a mixture of polar molecules, we may write

$$\bar{Q}(\omega)=\int_0^\infty \frac{\bar{G}(\tau)}{1+i\omega\tau}d\tau,$$
$$\overline{G(\tau)}=\int_0^\infty (n/\bar{n})G(\tau, n)\Phi(n)dn, \tag{55}$$

where $\Phi(n)dn$ is the fraction of the polymer molecules having a degree of polymerization between n and $n+dn$, and $G(\tau, n)$ is the relaxation time distribution function appropriate to a polymer of length n. According to Eqs. (51), (52) and (54), we may write

$$G(\tau, n)=\frac{1}{\tau_0}\frac{u}{(u+\tau/\bar{\tau}_0)^2},$$
$$u=n/\bar{n}\,;\quad \bar{\tau}_0=\bar{n}\tau^*. \tag{56}$$

In the usual polymerization reactions[8] without subsequent fractionation, the resulting distribution function $\Phi(n)$

$$\Phi(n)=e^{-n/\bar{n}}/\bar{n}. \tag{57}$$

Thus we may write

$$\bar{\tau}_0\bar{G}(\tau)=\int_0^\infty \frac{u^2}{(u+\tau/\bar{\tau}_0)^2}e^{-u}du, \tag{58}$$

TABLE I. *Reduced polarization from Eq. (60).*

x	$J(x)$	$H(x)$	x	$J(x)$	$H(x)$
100	0.0139	0.0313	1	0.415	0.2606
50	0.0263	0.0503	1/2	0.548	0.2652
30	0.0408	0.0696	1/3	0.620	0.2545
20	0.0570	0.0884	1/5	0.719	0.2328
10	0.0993	0.1279	1/10	0.822	0.1866
5	0.1637	0.1748	1/20	0.889	0.1400
3	0.230	0.2070	1/30	0.921	0.1136
2	0.290	0.2316	1/50	0.951	0.0849
			1/100	0.977	0.0547

[8] H. Mark, *High Polymers, II* (Interscience Publishers, New York), 1940.

which after integration gives

$$\bar{G}(\tau)=\frac{1}{\bar{\tau}_0}\left\{1+\left(\frac{\tau}{\bar{\tau}_0}\right)+\left(\frac{\tau}{\bar{\tau}_0}\right)\left(2+\frac{\tau}{\bar{\tau}_0}\right)\exp(\tau/\bar{\tau}_0)Ei(-\tau/\bar{\tau}_0)\right\}, \tag{59}$$

where $Ei(-\tau/\bar{\tau}_0)$ is the exponential integral. The real and imaginary parts of the reduced polarization $\bar{Q}(\omega)$ corresponding to the distribution function (59) are

$$J(x)=\int_0^\infty (1+x^2u^2)^{-1}\times[1+u+u(u+2)e^uEi(-u)]du,$$
$$H(x)=\int_0^\infty xu(1+x^2u^2)^{-1}\times[1+u+u(u+2)e^uEi(-u)]du, \tag{60}$$
$$x=\omega\bar{\tau}_0.$$

These functions have been calculated by numerical integration and are presented in Table I. The function $H(x)$ has a maximum at $x=0.63$ of 0.27, differing very little from the value 0.29 corresponding to a uniform degree of polymerization. The frequency of maximum loss ω_m is equal to $0.63/\bar{n}\tau^*$, thus inversely proportional to the average degree of polymerization. In Fig. 1, the reduced loss factor H is plotted as a function of $\log \omega/\omega_m$. Curve 1 represents the loss factor for a single relaxation time $1/\omega_m$, curve 2 the theoretical loss factor according to Eq. (60), and curve 3 the experimental loss factor for polyvinyl chloride plasticized with 20 percent diphenyl.

IV

No data on polymeric systems which are ideally suited for a comparison with the theory developed here are yet available. A qualitative comparison can be made in the case of polyvinyl chloride diphenyl systems[9] which have recently been investigated. These data include dielectric constant and loss-factor determinations over a wide range of temperature and frequency for

[9] Fuoss, unpublished results.

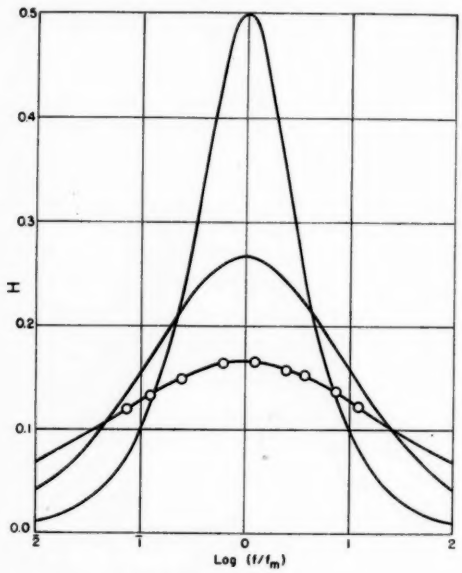

FIG. 1. Top curve, Debye function; center curve, function for dilute polydisperse linear polymer; bottom curve, *p*-vinyl chloride diphenyl, 80 : 20 at 50°.

polyvinyl chloride plasticized with 0–20 percent diphenyl. In general, the loss-factor temperature curves exhibit two maxima, and in the range of the high temperature maximum, the reduced loss-factor frequency curves can be represented empirically by the equation

$$H(f)=H_{\max}\ \text{sech}\ (\alpha \ln [f_m/f]),$$

where α is a distribution parameter, equal to unity for a system describable in terms of a single relaxation time and equal to zero for an infinitely wide distribution. It can be shown[3] that

$$H_{\max}=\alpha/2.$$

In Fig. 2 are shown values† of $H_{\max}$ as functions of composition at 50°, 60° and 70°; these values were obtained from the data by the method described in the preceding paper.[3] It will be seen that the experimental values are all smaller than the theoretical value of 0.267, which is shown as the dotted line in the figure. But in our calculation of the distribution function $G(\tau)$, each chain was assumed to act independently of its neighbors; in other words, a dilute solution of a polar polymer in a nonpolar solvent was implied, so that chain-chain interaction would be negligible. Qualitatively, we would expect a broadening of the distribution (and hence a lowering of $H_{\max}$) in concentrated solutions, because coupling of any sort between the chain molecules would superimpose another set of relaxation times on those characteristic of the single molecules. Experimentally, we find a definite trend of the values of H_m: with increasing diphenyl content at a given temperature, the observed values of H_m increase. Also, at a given composition, H_m increases with increasing temperature, which is what would be expected if increasing thermal motion decreased the mutual interaction of the chains. Finally, as pointed out in the previous section, no allowance for branching has been made: In neglecting it, another influence which would broaden $G(\tau)$ and hence decrease H_m has been omitted.

At present, we can only say that the agreement between theory and experiment is semi-quantitative, and that the deviations are in the direction anticipated, due to the differences between the physical system chosen as example and the model used in the calculation. Further work on more dilute solutions of linear polymers is planned.

APPENDIX I

Rotatory diffusion tensor of long chain molecule with skeletal bond angle of $\pi/2$

We shall consider only those configurations of the chain for which the center of gravity is fixed at its mean position at the midpoint of the central bond vector $\mathbf{a}_{n+1}$. If we denote by $\mathbf{R}_l$ the position of element l of the chain relative to the center of gravity, we may write for the velocity $\mathbf{v}_l$ of element l,

$$\mathbf{v}_l=\sum_{k=n+1}^{l-1}[\boldsymbol{\Omega}_k\times(R_l-R_k)]+(\boldsymbol{\Omega}_0\times\mathbf{R}_l),$$
$$\boldsymbol{\Omega}_K=\dot{\varphi}_K\mathbf{a}_K,\quad k>n+1 \qquad (1.1)$$
$$\boldsymbol{\Omega}_0=-\mathbf{i}(\sin\varphi)\dot{\vartheta}+\mathbf{j}(\cos\varphi)\dot{\vartheta}+\mathbf{k}\sin\vartheta\dot{\varphi},$$

where $\boldsymbol{\Omega}_k$ the vector angular velocity associated with the rotation about bond $\mathbf{a}_k$. If the elements are treated as hydrodynamically independent, of

† In principle, $H_{\max}$ can be determined from the values of the loss factor and dielectric constant at the frequency where the maximum in H appears, because the relationship $J=\frac{1}{2}$ where $H=H_{\max}$ evaluates the constant of proportionality between H and ϵ''. But for the polyvinyl chloride systems studied so far, this method is not applicable because the observed value of ϵ' in the high temperature range where H_m appears contains contributions from the mechanism which produces the low temperature maximum in ϵ'', and hence is too large.

resistance ρ, the element l experiences a force, $\mathbf{F}_l=\rho\mathbf{v}_l$, and a torque relative to the point of location of an arbitrary element s amounting to $\rho(\mathbf{R}_l-\mathbf{R}_s)\times\mathbf{v}_l$. The difference in total torque acting on elements $s+1, \cdots 2n$ and that acting on the elements $n+1, \cdots s-1$ is

$$\mathbf{T}_s=\rho\{\sum_{l=s+1}^{2n}(\mathbf{R}_l-\mathbf{R}_s)\times\mathbf{v}_l - \sum_{l=n+1}^{s-1}(\mathbf{R}_l-\mathbf{R}_s)\times\mathbf{v}_l\}. \quad (1.2)$$

Its component $(\mathbf{T}_s\cdot\mathbf{a}_s)$, which we will denote by T_s, is the scalar torque associated with the variable φ_s, and rotation around bond $\mathbf{a}_s$. Substitution of (1.1) in (1.2) and rearrangement of terms leads to the result

$$\begin{aligned} T_s&=\rho[\sum_{k=n+1}^{2n-1}\rho_{sk}\dot{\varphi}_k+\rho_{s0}\cdot\boldsymbol{\Omega}_0],\\ \rho_{sk}&=\sum_{l=k+1}^{2n}\mathbf{a}_s\cdot\boldsymbol{\gamma}_{skl}\cdot\mathbf{a}_k, \quad k\geqslant s\\ &=\sum_{l=s+1}^{2n}(\mathbf{a}_s\cdot\boldsymbol{\gamma}_{skl}\cdot\mathbf{a}_k)-\sum_{l=k+1}^{s-1}(\mathbf{a}_s\cdot\boldsymbol{\gamma}_{skl}\cdot\mathbf{a}_k);\\ &\qquad n+1\leqslant k\leqslant s-2 \quad (1.3)\\ \boldsymbol{\gamma}_{skl}&=[(\mathbf{R}_l-\mathbf{R}_k)\cdot(\mathbf{R}_l-\mathbf{R}_s)\mathbf{I}\\ &\qquad -(\mathbf{R}_l-\mathbf{R}_k)(\mathbf{R}_l-\mathbf{R}_s)],\\ \varrho_{s0}&=\sum_{l=s+1}^{2n}\mathbf{a}_s\cdot\boldsymbol{\gamma}_{s0l}-\sum_{l=n+1}^{s-1}\mathbf{a}_s\cdot\boldsymbol{\gamma}_{s0l}, \end{aligned}$$

where I is the unit dyadic. Applying the same considerations to the other half of the chain, and remembering that for $k<n$, $\boldsymbol{\Omega}_k=-\dot{\varphi}_k\mathbf{a}_k$, $T_k=-(\mathbf{T}_k\cdot\mathbf{a}_k)$, we obtain a similar result,

$$\begin{aligned} T_s&=\rho\{\sum_{k=1}^{n}\varrho_{sk}\dot{\varphi}_k+\varrho_{s0}\cdot\boldsymbol{\Omega}_0\},\\ \rho_{sk}&=\sum_{l=1}^{k-1}(\mathbf{a}_s\cdot\boldsymbol{\gamma}_{skl}\cdot\mathbf{a}_k); \quad k\geqslant s\\ &=\sum_{l=1}^{s-1}(\mathbf{a}_s\cdot\boldsymbol{\gamma}_{skl}\cdot\mathbf{a}_k)-\sum_{l=s+1}^{k-1}(\mathbf{a}_s\cdot\boldsymbol{\gamma}_{skl}\cdot\mathbf{a}_k);\\ &\qquad k>s+2 \quad (1.4)\\ \rho_{s0}&=-\sum_{l=1}^{s-1}\mathbf{a}_s\cdot\boldsymbol{\gamma}_{s0l}+\sum_{l=s+1}^{n}\mathbf{a}_s\cdot\boldsymbol{\gamma}_{s0l}, \end{aligned}$$

where the dyadics $\boldsymbol{\gamma}_{skl}$ have the same definition as in Eq. (1.3). The torque $\mathbf{T}_0$ associated with the variables ϑ and φ specifying the orientation of the middle bond in the system (**ijk**) is the total torque acting on the entire chain referred to the center of gravity at the midpoint of bond $\mathbf{a}_{n+1}$. This is

$$\begin{aligned} \mathbf{T}_0&=\rho\{\sum_{k=1}^{2n-1}\rho_{0k}\dot{\varphi}_k+\varrho_{00}\cdot\boldsymbol{\Omega}_0\},\\ \varrho_{0k}&=\sum_{l=n+1}^{2n}\boldsymbol{\gamma}_{0kl}\cdot\mathbf{a}_k; \quad k>n+1\\ &=-\sum_{l=1}^{n}\boldsymbol{\gamma}_{0kl}\cdot\mathbf{a}_k; \quad k<n, \quad (1.5)\\ \varrho_{00}&=\sum_{l=1}^{2n}[\mathbf{R}_l^2I-\mathbf{R}_l\mathbf{R}_l]. \end{aligned}$$

We have thus constructed the resistance tensor, ρ_{sk}, and in principle could construct the diffusion tensor

$$\begin{aligned} \mathbf{D}&=kT\varrho^{-1},\\ \dot{\varphi}_k&=\frac{1}{kT}\sum_{s=1}^{2n+1}D_{ks}T_s, \quad \text{etc.} \end{aligned} \quad (1.6)$$

This is prohibitively difficult for an arbitrary configuration of the chain. However, if we average the resistance tensor over all configurations of chain, with a skeletal bond angle of $\pi/2$, we find

$$\begin{aligned} \bar{\rho}_{sk}&=(\rho a^2/3)(n-|s-n|)^2\delta_{sk},\\ \bar{\varrho}_{00}&=2\rho a^2n^2I/3. \end{aligned} \quad (1.7)$$

This result follows from Eqs. (1.3, 1.4, 1.5) and an elementary calculation leading to the following

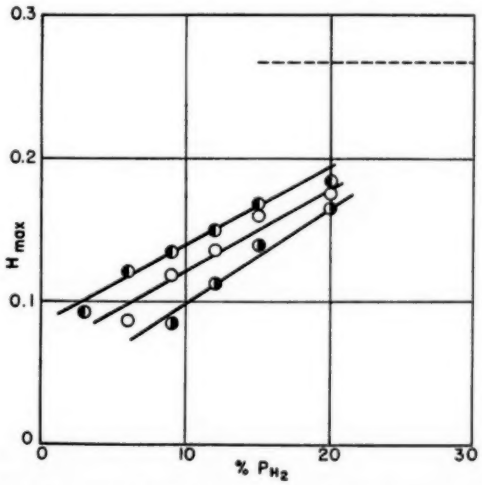

FIG. 2. Polyvinyl chloride diphenyl 80 : 20; open circle—60°; circle with left side filled in—70°, circle with right side filled in—50°. The dotted line is the theoretical value of H_m at infinite dilution.

average values,

$$\overline{\mathbf{a}_s\cdot\boldsymbol{\gamma}_{skl}\cdot\mathbf{a}_k}=(2a^2/3)\,|l-s|\,\delta_{ks};\quad l>s$$
$$=0;\quad l<s$$
$$\overline{\mathbf{i}\cdot\boldsymbol{\gamma}_{skl}\cdot\mathbf{a}_k}=\overline{\mathbf{j}\cdot\boldsymbol{\gamma}_{skl}\cdot\mathbf{a}_k}=\overline{\mathbf{k}\cdot\boldsymbol{\gamma}_{skl}\cdot\mathbf{a}_k}=0, \tag{1.8}$$
$$\overline{\mathbf{R}_l\cdot\mathbf{R}_s}=a^2|l-n|;\quad \mathbf{R}_l\mathbf{R}_s=(a^2/3)\,|l-n|\,I;\quad \begin{cases} l>n;\ l<s \\ l<n;\ l>s \end{cases}$$
$$\overline{\mathbf{R}_l\cdot\mathbf{R}_s}=a^2|s-n|;\qquad =(a^2/3)\,|s-n|\,I;\quad \begin{cases} l>n;\ l>s \\ l<n;\ l<s \end{cases}$$

where a is the bond length. The diagonal diffusion tensor, Eq. (29) follows at once from Eq. (1.7).

Appendix II

Calculation of the coefficients $\beta_\lambda^{(l)}$ in the expansion of the $\beta^{(l)}$ in the eigenfunctions ψ_λ

We shall consider in detail only the case $l>n+1$. The case $l<n$ may be treated in a similar manner. From Eqs. (28) and (29), we have,

$$\beta_\lambda^{(l)}=(3/4\pi)^{\frac{1}{2}}(2\pi)^{-(2n-1)/2}\mathbf{k}\cdot\boldsymbol{\Lambda}_0(\gamma)\times\prod_{s=l-1}^{n+1}\boldsymbol{\Lambda}(\gamma,\varphi_s)\boldsymbol{\Lambda}(\vartheta,\varphi)\cdot\mathbf{k}, \tag{2.1}$$
$$\psi_\lambda=\left[\left(\frac{2K+1}{2}\right)\frac{(K-|m|)!}{(K+|m|)!}\right]^{\frac{1}{2}}(2\pi)^{-(2n+1)/2}\times P_K^m(\cos\vartheta)e^{im\varphi}\prod_{s=1}^{2n-1}e^{im_s\varphi_s}.$$

When the supplement γ of the bond angle is $\pi/2$, Eq. 26 yields

$$\boldsymbol{\Lambda}=\boldsymbol{\Lambda}_0+\boldsymbol{\Lambda}_+e^{i\varphi}+\boldsymbol{\Lambda}_-e^{-i\varphi},$$
$$\boldsymbol{\Lambda}_0=-\mathbf{k}i,$$
$$\boldsymbol{\Lambda}_\pm=\tfrac{1}{2}[\mathbf{j}(\mathbf{j}\pm\mathbf{k})+\mathbf{i}(\mathbf{k}\mp\mathbf{j})], \tag{2.2}$$
$$\boldsymbol{\Lambda}(\vartheta,\varphi)\cdot\mathbf{k}=(\mathbf{i}+\mathbf{j})\tfrac{1}{2}\sin\vartheta e^{i\varphi}+(\mathbf{i}-\mathbf{j})\tfrac{1}{2}\sin\vartheta e^{-i\varphi}+\mathbf{k}\cos\vartheta.$$

We first compute the coefficient $[\boldsymbol{\Lambda}(\vartheta,\varphi)\cdot\mathbf{k}]_{K,m}$

$$[\boldsymbol{\Lambda}(\vartheta,\varphi)\cdot\mathbf{k}]_{Km}=\left(\frac{4\pi}{3}\right)^{\frac{1}{2}}\left\{\frac{\mathbf{i}+\mathbf{j}}{\sqrt{2}}\delta_{m,1}+\frac{\mathbf{i}-\mathbf{j}}{\sqrt{2}}\delta_{m,-1}+\mathbf{k}\delta_{m,0}\right\}\delta_{K,1}. \tag{2.3}$$

We next compute the coefficient $[\boldsymbol{\Lambda}(\gamma,\varphi_s)]_{m_s}$,

$$[\boldsymbol{\Lambda}(\gamma,\varphi_s)]_{m_s}=(2\pi)^{\frac{1}{2}}\{\boldsymbol{\Lambda}_0\delta_{m_s,0}+\boldsymbol{\Lambda}_+\delta_{m_s,1}+\boldsymbol{\Lambda}_-\delta_{m_s,-1}\}. \tag{2.4}$$

The expansion coefficients of unity are $(2\pi)^{\frac{1}{2}}\delta_{m_s,0}$. Substitution of (2.3) and (2.4) in Eq. (2.1) yields

$$\beta_\lambda^{(l)}=\left(\prod_{s=1}^{n}\delta_{m_s,0}\right)\left(\prod_{s=l}^{2n-1}\delta_{m_s,0}\right)\delta_{K,1}\mathbf{k}\cdot\boldsymbol{\Lambda}_0\times\prod_{s=l-1}^{n+1}\{\boldsymbol{\Lambda}_0\delta_{m_s,0}+\boldsymbol{\Lambda}_+\delta_{m_s,1}+\boldsymbol{\Lambda}_-\delta_{m_s,-1}\}$$
$$\times\left\{\mathbf{i}\frac{\delta_{m,1}+\delta_{m,-1}}{\sqrt{2}}+\mathbf{j}\frac{\delta_{m,1}-\delta_{m,-1}}{\sqrt{2}}+\mathbf{k}\delta_{m,0}\right\}. \tag{2.5}$$

Since $\boldsymbol{\Lambda}_0^2$ vanishes according to Eq. (2.2) no neighboring elements s can both have their $m_s=0$. Thus all nonvanishing products of the type (2.5) will have the form,

$$\beta_\lambda^{(l)}=\mathbf{k}\cdot\boldsymbol{\Lambda}_0\boldsymbol{\Lambda}_\pm^{r_1}\boldsymbol{\Lambda}_0\boldsymbol{\Lambda}_\pm^{r_2}\cdots\boldsymbol{\Lambda}_\pm^{r_\alpha}\times\{\boldsymbol{\Lambda}_0\delta_{m_s,0}+\boldsymbol{\Lambda}_+\delta_{m_s,1}+\boldsymbol{\Lambda}_-\delta_{m_s,-1}\}\cdot\left\{\mathbf{i}\frac{\delta_{m,1}+\delta_{m,-1}}{\sqrt{2}}+\mathbf{j}\frac{\delta_{m,1}-\delta_{m,-1}}{\sqrt{2}}+\mathbf{k}\delta_{m,0}\right\}, \tag{2.6}$$
$$\sigma=r_1+r_2+\cdots=\sum_{s=n+1}^{l-1}m_s^2.$$

Now it is readily verified by construction of the products with use of Eq. (2.2) that

$$|\mathbf{k}\boldsymbol{\Lambda}_0\boldsymbol{\Lambda}_\pm^{r_1}\cdots\boldsymbol{\Lambda}_\pm^{r_\alpha}\cdot\boldsymbol{\Lambda}_0|=2^{-\sigma}\mathbf{i},$$
$$|\mathbf{k}\cdot\boldsymbol{\Lambda}_0\boldsymbol{\Lambda}_\pm^{r_1}\boldsymbol{\Lambda}_0\cdots\boldsymbol{\Lambda}_\pm^{r_\alpha}\boldsymbol{\Lambda}_\pm|=2^{-\sigma}(\mathbf{j}\mp\mathbf{k}). \tag{2.7}$$

Substitution Eq. (2.7) in Eq. (2.6) yields Eq. (32) for $|\beta_\lambda^{(l)}|$.

Dispersion and Absorption in Dielectrics

I. Alternating Current Characteristics*

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(Received February 4, 1941)

The dispersion and absorption of a considerable number of liquid and dielectrics are represented by the empirical formula

$$\epsilon^*-\epsilon_\infty=(\epsilon_0-\epsilon_\infty)/[1+(i\omega\tau_0)^{1-\alpha}]. \quad (1)$$

In this equation, ϵ^* is the complex dielectric constant, ϵ_0 and ϵ_∞ are the "static" and "infinite frequency" dielectric constants, $\omega=2\pi$ times the frequency, and τ_0 is a generalized relaxation time. The parameter α can assume values between 0 and 1, the former value giving the result of Debye for polar dielectrics. The expression (1) requires that the locus of the dielectric constant in the complex plane be a circular arc with end points on the axis of reals and center below this axis.

If a distribution of relaxation times is assumed to account for Eq. (1), it is possible to calculate the necessary distribution function by the method of Fuoss and Kirkwood. It is, however, difficult to understand the physical significance of this formal result.

If a dielectric satisfying Eq. (1) is represented by a three-element electrical circuit, the mechanism responsible for the dispersion is equivalent to a complex impedance with a phase angle which is independent of the frequency. On this basis, the mechanism of interaction has the striking property that energy is conserved or "stored" in addition to being dissipated and that the ratio of the average energy stored to the energy dissipated *per cycle* is independent of the frequency.

I. INTRODUCTION

IT is a familiar fact that the dielectric constants of many liquids and solids depend markedly on the frequency of measurement. The dependence is in general found to be a decrease from a static value ϵ_0 at low frequencies to a smaller limiting value ϵ_∞ at higher frequencies. In the transition region of anomalous dispersion there is an "absorption conductivity" and the situation may be described in terms of a complex dielectric constant $\epsilon^*=\epsilon'-i\epsilon''$.

The classical theory of the effect for polar liquids is due to Debye.[1] In this theory the difference between the values ϵ_0 and ϵ_∞ is attributed to dipole polarization. The orientation of polar molecules in an alternating-current field is opposed by the effects of thermal agitation and molecular interactions. Debye represents the second effect by a picture of viscous damping, the molecules being regarded as spheres in a continuous medium having the macroscopic viscosity. The theoretical analysis in this case leads to the equation[2]

$$\epsilon^*-\epsilon_\infty=(\epsilon_0-\epsilon_\infty)/(1+i\omega\tau_0), \quad (1)$$

which can be written

$$\epsilon'-\epsilon_\infty=(\epsilon_0-\epsilon_\infty)/[1+(\omega\tau_0)^2],$$
$$\epsilon''=(\epsilon_0-\epsilon_\infty)\omega\tau_0/[1+(\omega\tau_0)^2], \quad (2)$$

where $\omega=2\pi\cdot$frequency and the parameter τ_0 is a characteristic constant which may be called the relaxation time.[3]

Dispersion and absorption can also occur in nonhomogeneous dielectrics. The possibility of absorption in a double-layer dielectric if the ratios of conductivities and dielectric constants of the two layers are not equal was first pointed out by Maxwell.[4] Wagner[5] has derived expressions for ϵ', ϵ'' in the case of spheres dispersed in a uniform dielectric medium. These expressions are

* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.

[1] P. Debye, *Polar Molecules* (Chemical Catalogue Company, New York, 1929).

[2] Reference 1, p. 94.

[3] This constant τ_0 is not the same as the relaxation time as defined by Debye, differing from it by a constant factor which depends on the theory assumed for the static dielectric constant, cf. R. H. Cole, J. Chem. Phys. **6**, 385 (1938). The distinction is unimportant for the present discussion.

[4] J. C. Maxwell, *Electricity and Magnetism* (Oxford Press, London, 1892), Vol. I.

[5] K. W. Wagner, Ann. d. Physik **40**, 817 (1913).

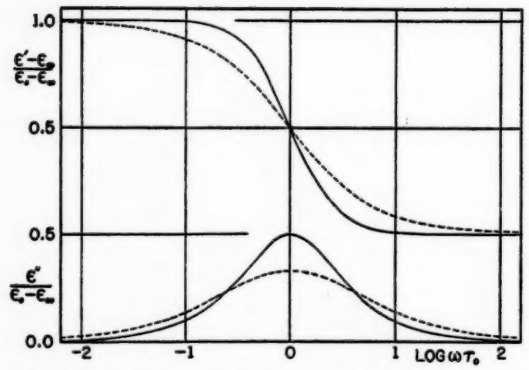


FIG. 1. Real and imaginary parts of the dielectric constant plotted against frequency. The solid curves are for the Debye Eqs. (2), the dashed curves indicate the type of behavior frequently found experimentally.

identical in form with Eqs. (2), differing only in the significance of the parameters ϵ_0, ϵ_∞, and τ_0.

Theories of other types of dispersion phenomena also lead to equations of the same type form. The simple theories of paramagnetic dispersion as developed by Gorter and Kronig,[6] and Casimir and du Pre,[7] are examples. The same frequency dependence of elastic dispersion and damping in metals subjected to alternating stress is predicted by the theory of Zener.[8]

One might thus expect these relations to have a very general validity as a description of dispersion processes. Nevertheless, there is a considerable amount of experimental evidence to indicate that Eqs. (2) are not a correct description of the observed frequency dependence in such processes. The observed behavior is rather generally found to consist in a considerably broader frequency range of dispersion and absorption together with a smaller maximum value of ϵ'' than is predicted by Eqs. (2). This is particularly true in the case of liquid and solid dielectrics, and it is the purpose of the present paper to present the results of an analysis of representative experimental data.

The steady state response of a dielectric or other dispersion system to a sinusoidal force as a function of frequency is formally related to the transient response to an applied force as a function of time by a Fourier integral. A complete knowledge of either response is sufficient to determine the other. The discharge of a condenser containing a dielectric described by Eq. (1) follows the familiar exponential decay curve. If Eq. (1) is not an adequate description of the steady state properties, it follows that the transient response must differ from the predicted exponential time dependence and vice versa. Such deviations are indeed found experimentally in many cases. The significance of the observed behavior and its relation to the steady state characteristics will be considered in a later paper.[9]

II. Representation of Dispersion Data

Before discussing the applicability of Eq. (2) to dielectric constant data it is worth while to consider the possible representations of such data. Ordinarily it is customary to plot ϵ' and either ϵ'' or the loss factor $\tan\delta(=\epsilon''/\epsilon')$ against the frequency or wave-length. If the Debye Eqs. (2) are valid, one obtains the solid curves of Fig. 1, the symmetry resulting from the logarithmic frequency scale. The experimental data often possess this same type of logarithmic symmetry but with the important differences that the frequency range of dispersion is broader and the absorption smaller in maximum value. This behavior is indicated by the dashed curves in Fig. 1.

The experimental data are not readily analyzed by such a representation nor is the significance of departures from the expected behavior easily appreciated. A more convenient basis for discussion is the Argand diagram or complex plane locus in which the imaginary part of the complex dielectric constant is plotted against the real part, each point being characteristic of one frequency of measurement. The locus of Eqs. (2) in this representation is a semicircle with its center on the real (ϵ') axis and intercepts at ϵ_0 and ϵ_∞ on this axis. This is easily shown from Eq. (1) which can be written in the form $u+v=\epsilon_0-\epsilon_\infty$, where $u=\epsilon^*-\epsilon_\infty$, $v=i\omega\tau_0(\epsilon^*-\epsilon_\infty)$. The quantities u, v, considered as vectors in the complex plane are perpendicular, their vector sum being the constant real quantity $\epsilon_0-\epsilon_\infty$. The right angle in-

[6] C. J. Gorter and R. de L. Kronig, Physica **3**, 1009 (1936).
[7] H. B. G. Casimir and F. K. du Pre, Physica **5**, 507 (1938).
[8] C. Zener, Phys. Rev. **53**, 90 (1938).
[9] "Dispersion and absorption in dielectrics. II. Direct current characteristics," to be submitted to this journal.

cluded by these vectors is therefore inscribed in a semicircle of diameter $\epsilon_0-\epsilon_\infty$, as shown in Fig. 2 (a) (the imaginary part of ϵ^* is plotted as positive). This semicircle is then the locus of the dielectric constant as ω varies from 0 to ∞. This circle diagram has proved a very convenient representation of dispersion data in general.[10] Its usefulness for the present subject of discussion will be evident from what follows.

The complex plane locus suffers from the seeming disadvantage that both real and imaginary parts of the dielectric constant must be known if the data are to be analyzed in this fashion. This difficulty is more apparent than real, however, as an experimental method suitable for determination of either component usually involves a determination of the other as well. It is important, moreover, to realize that one cannot say whether or not the Debye equations are in adequate description of the facts unless these data or their equivalent are available (see, however, under IV). The discussion of the following section is therefore concerned with an analysis of some reasonably complete dispersion and absorption data in the literature. The conclusions which can be drawn from less complete data will be considered in V.

III. Experimental Evidence

A. Liquids

The original Debye theory of dispersion and absorption was developed for polar gases and dilute solutions of polar liquids, but has been extensively applied to results on pure polar liquids. The major difficulty in testing it adequately lies in the technical problem of making measurements at the necessary frequencies of 10^8 to 10^{11} cycles for simple polar liquids. It is important to note that for liquids one usually knows both ϵ_0 and ϵ_∞, the former from low frequency measurements and the latter by extrapolation to zero frequency of the optical index of refraction.[11] If these end points are known, the semicircle is completely defined, except that knowledge of ϵ_0 and ϵ_∞ obviously does not determine the frequency range in which the effects occur.

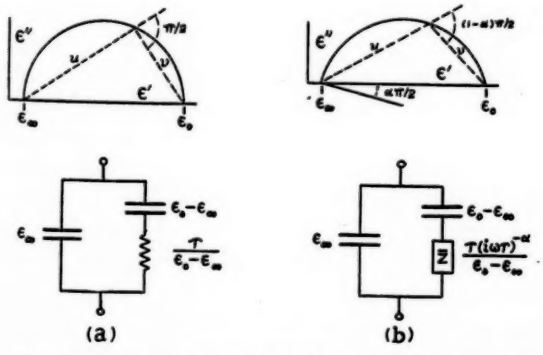


FIG. 2. Theoretical complex plane loci of the complex dielectric constant and equivalent circuits for dielectrics; (a) Debye theory, (b) as required by experimental evidence.

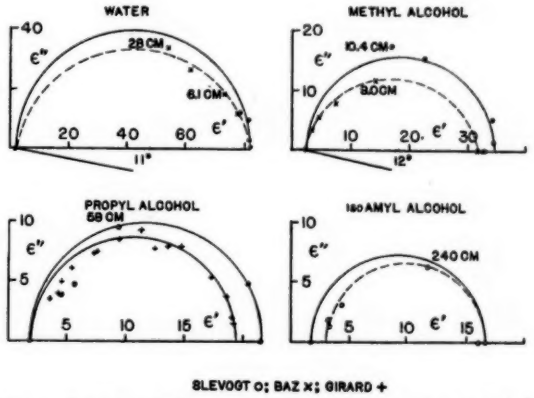


FIG. 3. Complex dielectric constants of water and alcohols.

Bäz,[12] and Slevogt,[13] have made measurements on water, methyl and ethyl alcohols over the frequency ranges 3×10^9c-10^{10}c and 10^8c-3×10^9c, respectively. The dielectric constant data for water and methyl alcohol are plotted in the complex plane in Fig. (3). It is evident that the data are not in good agreement nor do they establish the validity of the theoretical semicircle. The same thing is true of the results for ethyl alcohol. Slevogt has also measured several of the higher alcohols. His data for propyl alcohol, together with values given by Girard,[14] are plotted in Fig. (3). The internal consistency and

[10] See, for example, K. S. Cole, J. Gen. Physiol. **12**, 29 (1928); *ibid.* **15**, 641 (1932).

[11] This procedure is not without uncertainty because of the possibility of atomic polarization giving rise to absorption in the infra-red and a related dispersion of which this extrapolation takes no account. In the absence of definite information on this point, one can do no better than to ignore the difficulty. The error should not, in most cases, be serious.

[12] G. Bäz, Physik. Zeits. **40**, 394 (1939).

[13] K. E. Slevogt, Ann. d. Physik **36**, 141 (1939).

[14] P. Girard, Trans. Faraday Soc. **30**, 763 (1934).

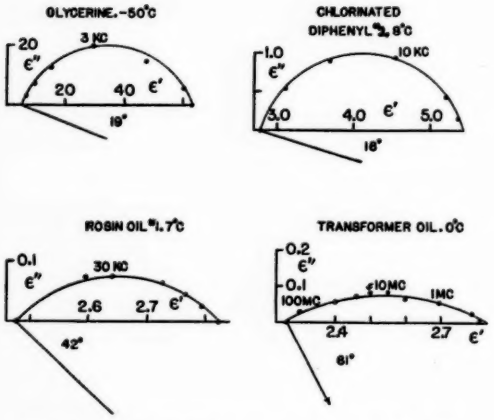
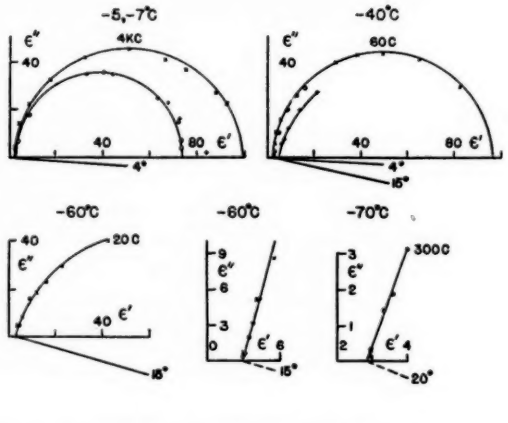


FIG. 4. Complex dielectric constants of liquids.



MURPHY ×, SMYTH AND HITCHCOCK ○, WINTSCH +.

FIG. 5. Complex dielectric constants of ice at various temperatures.

agreement of the two sets of data are seen to be rather poor in this case also. Slevogt's results for *n*-amyl alcohol, as plotted in Fig. 3, can be fitted by a semicircle only if ϵ_∞ is taken to be 3.1 rather than the value 1.9 corresponding to the square of the optical index of refraction. This difference can be plausibly explained as being due to atomic polarization. However, the internal consistency of the data is sufficiently poor that this explanation is only a tentative one. This effect is not indicated for methyl and ethyl alcohols on the basis of Bäz' data and it is not possible to fit a semicircle to his results. They can, however, be represented quite well by a circular arc with center below the ϵ' axis as shown in Fig. 3. This type of departure from the predictions of the simple dispersion theories is characteristic of a large number of dielectrics, as will be evident from the discussion of the succeeding sections. It is apparent that no definite conclusions are justified in the case of polar liquids on the basis of data similar to those discussed in this section. There is, therefore, a great need for reliable values of ϵ' and ϵ'' for polar liquids at frequencies which cover the major part of the dispersion range.

On the basis of the Debye theory one should expect the dispersion range to occur at much lower frequencies for viscous liquids, as the relaxation time is proportional to the quotient η/T, where η is the macroscopic viscosity and T is the absolute temperature. This type of dependence is found experimentally in many cases. The dispersion effect may thus occur in a much more convenient frequency range and quite complete data exist in the literature for liquids such as glycerine and various glycols which are extremely viscous at sufficiently low temperatures. The dispersion range for insulating oils may also occur at experimentally convenient frequencies. In some cases, it is doubtful as to whether the dispersion for such liquids is due to dipole polarization. Examples of this latter type need not be excluded from the present discussion because, as already mentioned, all the simple dispersion theories predict the same frequency dependence. A detailed theory must, of course, take this difference into account.

Morgan,[15] has measured ϵ', ϵ'' for glycerine at temperatures down to -70°C and over the frequency range $30c-10^5c$. The complex plane locus at -50°C is plotted in Fig. 4 from data obtained by interpolation on his published plots of ϵ', ϵ'' against the temperature. It is apparent that the experimental results cannot be represented satisfactorily by a semicircle but that a circular arc with depressed center is a good approximation.

Data of White and Morgan,[16] for a chlorinated diphenyl, also plotted in Fig. 4, were obtained in the same way and show the same effect. The characteristic departure from the semicircle is found to an even greater extent in data for a

[15] S. O. Morgan, Trans. Electrochem. Soc. **65**, 109 (1934).
[16] A. H. White and S. O. Morgan, J. Frank. Inst. **216**, 635 (1933).

rosin oil[17] and a transformer oil,[18] which are also plotted in Fig. 4. It is to be noted that the dispersion range of frequencies is much wider and the maximum absorption much smaller in such cases.

The circular arc locus is found to be an excellent representation of data on a considerable number of other liquids for which data are available. It is useful to have some simple measure of the departure of such arcs from a semicircle. This is conveniently taken to be the angle between the ϵ' axis and the radius of the arc drawn to the point ϵ_∞, and the value of this angle is indicated on the plots in Figs. 3 and 4.

B. Solids

One should expect the parameter τ_0 to be much larger for polar solids than for polar liquids and the frequency range of dispersion to be a more convenient one as a result. Experimentally, however, the situation often turns out to be no simpler because this frequency range is often as awkwardly low as that for liquids is high. In such cases there is a difficulty not found for liquids in that the static dielectric constant is now an unknown quantity the value of which can be inferred only by extrapolation of the dispersion curve to zero frequency. There are, however, some reasonably complete data on dispersion in crystalline polar solids which are suitable for the present purpose.

Dielectric constants for ice have been determined over a considerable temperature and frequency range by Wintsch,[19] Smyth and Hitchcock,[20] and Murphy.[21] Some of their results are plotted in Fig. 5. The data of Wintsch and of Murphy extend to lower frequencies so that a more complete picture of the dispersion is afforded than by the results of Smyth and Hitchcock. It is again evident from these graphs that a circular arc rather than a semicircle is consistent with the experimental data, particularly at the lower temperatures. The data of Smyth and Hitchcock at temperatures below $-30°$C are not complete enough to permit one to infer the nature of the complete locus. It is, however, significant that the data are not consistent with the assumption of a semicircle. It is seen from Fig. 5 that the data require that the dielectric constant locus approach the ϵ' axis at an angle of somewhat less than 90°. At these "low" frequencies the data are thus consistent with the circular arc locus found in the other examples.

White, Biggs and Morgan,[22] have shown that several crystalline benzene derivatives exhibit dispersion and absorption in the frequency range 1 to 100 kc. Some of their data at temperatures for which this frequency range gives a fairly complete picture are plotted in Fig. 6. In these cases also, the circular arc is an excellent representation of the data. All the data of these workers which show appreciable dispersion also show considerable deviations from the semicircular locus. These deviations increase with decreasing temperature and, as far as can be determined

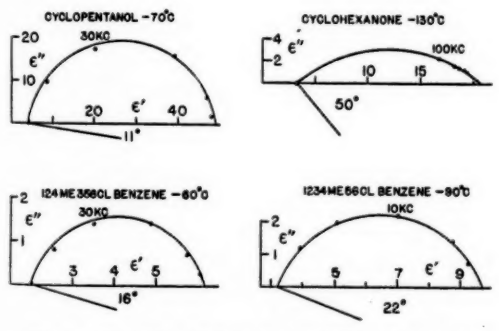


FIG. 6. Complex dielectric constants of organic crystalline solids.

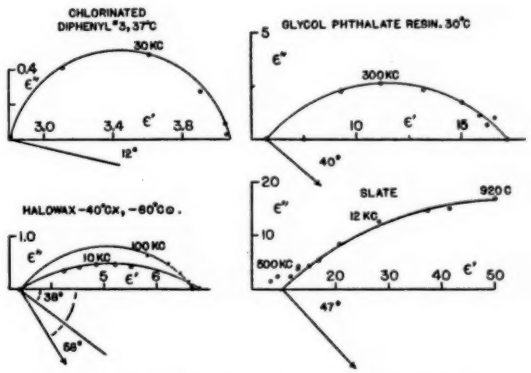


FIG. 7. Complex dielectric constants of solids.

[17] S. O. Morgan and A. H. White, J. Frank. Inst. **213**, 313 (1932).
[18] H. Rieche, Zeits. f. Physik **95**, 158 (1935).
[19] H. Wintsch, Helv. Phys. Acta **5**, 126 (1932).
[20] C. P. Smyth and C. S. Hitchcock, J. Am. Chem. Soc. **54**, 4631 (1932).
[21] E. J. Murphy, Trans. Electrochem. Soc. **65**, 309 (1934).
[22] A. H. White, S. S. Biggs and S. O. Morgan, J. Am. Chem. Soc. **62**, 16 (1940).

from the data presented graphically, the results are well fitted by a circular arc.

White and Bishop[23] have made measurements on a large number of organic crystals and have found dispersion in many cases. Their values for cyclopentanol at $-70°C$ and cyclohexanone at $-130°C$ are plotted in Fig. 6 and again one finds that circular arcs are required to fit the data. Other results reported in the same paper show similar dispersion characteristics, and it is reasonable to conclude that the circular arc is an excellent analytic representation of the dispersion in a variety of organic crystals.

Data are available in the literature for a number of solid dielectrics of interest in insulation problems. These dielectrics are usually of complex and uncertain molecular composition, and one might not expect to find any very close similarities in their dispersion characteristics. It turns out, however, that the circular arc locus is a very general expression of data for these dielectrics. Four examples are shown in Fig. 7.[24]

No detailed comment is necessary on the general characteristics, which are sufficiently evident from Fig. 7. It should, however, be pointed out that for such dielectrics as these the departures from the semicircle are very great in many cases, but that these departures are nevertheless represented by a circular arc. It is thus evident from these examples and the ones previously discussed that this type of locus is characteristic of a large number of otherwise dissimilar dielectrics.

IV. Other Statements of the Experimental Results

A. Analytic formulation

The analytical expression for the circular arc locus is easily deduced by consideration of Fig. 2. From simple geometry the angle $(1-\alpha)\pi/2$ between the vectors u and v in the complex plane is independent of the frequency and equal to half the central angle subtended by the arc. It therefore follows that

$$u+v=u[1+f(\omega)e^{i(1-\alpha)\pi/2}]=\epsilon_0-\epsilon_\infty, \qquad (3)$$

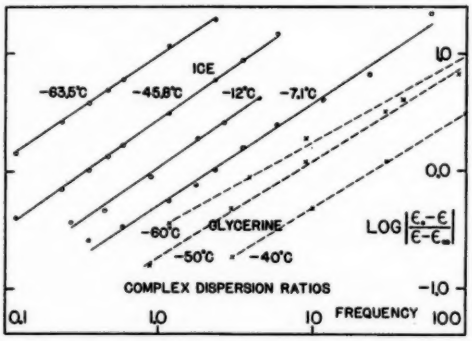


FIG. 8. Frequency dependence of the complex dielectric constants of ice and glycerine, as explained in the text. The logarithmic scales of frequency have been shifted by arbitrary amounts.

where $f(\omega)$ is a (real) undetermined function of the frequency and other parameters. From the relation $e^{i(1-\alpha)\pi/2}=i^{(1-\alpha)}$ this can be written

$$\epsilon^*-\epsilon_\infty=(\epsilon_0-\epsilon_\infty)/[1+i^{(1-\alpha)}f(\omega)], \qquad (4)$$

as the complex quantity u is simply $\epsilon^*-\epsilon_\infty$, where ϵ^* is the complex dielectric constant.

The dependence of the function $f(\omega)$ on the frequency is undetermined by this geometrical argument. From general considerations one can expect that this dependence will be of the form $\omega^{1-\alpha}$, as the complex form of ϵ^* results from the initial hypothesis of an applied field $E=E_0e^{i\omega t}$. Any theory in which ω appears as the result of linear operations on the complex exponential must lead to the same functional dependence on ω as on the unit imaginary i so that

$$\epsilon^*-\epsilon_\infty=(\epsilon_0-\epsilon_\infty)/[1+(i\omega\tau_0)^{1-\alpha}], \qquad (5)$$

where the parameter τ_0 is left undetermined.

This dependence of $f(\omega)$ on ω is easily verified from the experimental data by plotting the logarithm of the ratio $|v/u|$ against the logarithm of the frequency. It is easily shown from Eq. (5) that

$$|v/u|=(\omega\tau_0)^{1-\alpha}, \qquad (6)$$

and the locus of $\log_e|v/u|$ plotted against $\log_e\omega$ is a straight line of slope $1-\alpha$.[25] As an illustration, these quantities are plotted from the data of Murphy for ice and of Morgan for glycerine in Fig. 8. It is seen that the locus is indeed a straight line of slope less than unity as required by Eq. (6). Furthermore, the values of α

[23] A. H. White and W. S. Bishop, J. Am. Chem. Soc. **62**, 8 (1940).

[24] The sources of the data are: chlorinated diphenyl, reference 16; glycol phthalate resin, W. A. Yager, Physics **7**, 434 (1936); Halowax, reference 15; slate, G. E. Bairsto, Proc. Roy. Soc. **96**, 363 (1920).

[25] K. S. Cole, J. Gen. Physiol. **12**, 29 (1928).

so obtained are in agreement with the values required by the circular arc loci.

The real and imaginary parts ϵ', ϵ'' of the complex dielectric constant as a function of frequency are given by

$$\epsilon'-\epsilon_\infty=\frac{(\epsilon_0-\epsilon_\infty)[1+(\omega\tau_0)^{1-\alpha}\sin\tfrac{1}{2}\alpha\pi]}{1+2(\omega\tau_0)^{1-\alpha}\sin\tfrac{1}{2}\alpha\pi+(\omega\tau_0)^{2(1-\alpha)}}$$

$$=\tfrac{1}{2}(\epsilon_0-\epsilon_\infty)\left[1-\frac{\sinh(1-\alpha)x}{\cosh(1-\alpha)x+\cos\tfrac{1}{2}\alpha\pi}\right],$$

$$\epsilon''=\frac{(\epsilon_0-\epsilon_\infty)(\omega\tau_0)^{1-\alpha}\cos\tfrac{1}{2}\alpha\pi}{1+2(\omega\tau_0)^{1-\alpha}\sin\tfrac{1}{2}\alpha\pi+(\omega\tau_0)^{2(1-\alpha)}}$$

$$=\frac{\tfrac{1}{2}(\epsilon_0-\epsilon_\infty)\cos\tfrac{1}{2}\alpha\pi}{\cosh(1-\alpha)x+\sin\tfrac{1}{2}\alpha\pi}, \tag{7}$$

where $x=\log_e(\omega\tau_0)$. It is easily seen that Eqs. (7) reduce to the Debye expressions (2) for $\alpha=0$. For values of α greater than zero the dispersion region is broader and the maximum value of ϵ'' for $\omega=1/\tau_0$ decreased.

If data are available only for ϵ' or ϵ'' alone as a function of frequency, the applicability of Eq. (5) can be determined by some such method as comparison with standard curves for Eq. (7). It should be noted that ϵ' and ϵ'' are uniquely determined if either ϵ' or ϵ'' is known over the entire frequency range for which dispersion and absorption occur. The general relations

$$\epsilon'(\omega)-\epsilon_\infty=-\frac{2}{\pi}\int_0^\infty\frac{\epsilon''(\nu)\nu d\nu}{\nu^2-\omega^2},$$

$$\epsilon''(\omega)=\frac{2}{\pi}\int_0^\infty\frac{[\epsilon'(\nu)-\epsilon_\infty]\omega d\nu}{\nu^2-\omega^2}, \tag{8}$$

were given by Kramers[26] and are easily shown to follow from the fact that ϵ' and ϵ'' are conjugate functions. It is readily verified that the relations (8) are satisfied by the explicit forms of ϵ' and ϵ'' given in Eqs. (7).

B. Equivalent circuits

It is often convenient to represent the properties of dielectrics exhibiting dispersion by means of an equivalent electrical circuit. Such a network for a dielectric described by an equation of the Debye form is shown in Fig. 2(a). In this circuit the capacity ϵ_∞ represents the polarization which is established even at very high frequencies, while the capacity $\epsilon_0-\epsilon_\infty$ corresponds to the polarization set up only for low frequencies of the field. The mechanism which acts to prevent this polarization from being established at higher frequencies is represented by the resistance $\tau_0/(\epsilon_0-\epsilon_\infty)$.

If the experimental data require the circular arc locus and Eq. (5) as an expression of the dispersion, the resistance of Fig. 2(a) is replaced by a complex impedance $Z=\tau_0(i\omega\tau_0)^\alpha/(\epsilon_0-\epsilon_\infty)$. This impedance has the striking property that, while the resistance and reactance components are functions of the frequency, the phase angle is a constant independent of the frequency and equal to $\frac{1}{2}\alpha\pi$.

Since the angle between the ϵ' axis and the radius vector to the point ϵ_∞ of the circular arc in the complex plane locus is also equal to $\frac{1}{2}\alpha\pi$, the properties of a dielectric with a locus of this kind may be stated equally well in terms of this phase angle or in terms of the index α. It must be understood that the use of the complex impedance Z is merely one way of expressing the experimental facts and that it and its real and imaginary parts have no conventional meaning.

V. Interpretation of Less Complete Dispersion Data

In many cases dispersion data given in the literature are not sufficiently complete to determine uniquely the complete dependence of the complex dielectric constant on the frequency. It is, however, possible in some cases to show definitely that such data are consistent with Eq. (5) and not with Eq. (1).

A. The complex plane locus for very low or high frequencies

Because of technical difficulties, experimental values of ϵ' and ϵ'' are sometimes known only near the low or high frequency limit of the dispersion range so that the complete dielectric constant locus cannot be plotted. In these cases it is possible only to determine whether Eqs. (1) or (5) are consistent with the data. If Eq. (1) is valid, the locus approaches the ϵ' axis for $\omega=0$ or

[26] H. A. Kramers, Atti Congr. dei Fisici, Como, 545, 1927. See also reference 6.

TABLE I. *Constants of dispersion and absorption for various dielectrics.**

	T°C	ϵ_0	ϵ_∞	a	b	α	REFERENCE
		A: Liquids					
Water	19	81	1.8	9.4	12	0.09	12
Water	19	81	1.8	——		(0.0)	13
Methyl alcohol	19	31.8	2.0	6.4	11	0.13	12
	19	(33.2)	2.0	5.9	11	(0.0)	13
Ethyl alcohol	20	25.8	1.85	9.4	11	0.15	12
	19	26.0	1.85	1.3	10	(0.0)	13
Propyl alcohol	?	19.2	1.9	3.2	10	(0.0)	14
	19	21.3	1.9	3.2	10	(0.0)	13
n-Butyl alcohol	19	19.1	(3.2)	6.4	10	(0.0)	13
Iso-amyl alcohol	19	(16.1)	(3.1)	1.0	9	(0.0)	13
Glycerine	−50	63	5.0	6.9	5	0.21	15
	−60	69	5.0	1.2	3	0.21	15
Rosin oil No. 1	7	2.825	2.475	3.8	6	0.46	17
	−1	2.840	2.475	1.9	5	0.51	17
	−5	2.858	2.475	6.4	5	0.53	17
Rosin oil No. 2	−40	2.67	2.48	2.9	5	0.37	17
	−50	—	2.48	——		(0.64)	17
Transformer oil	0	2.82	2.26	2.0	8	0.63	18
Chlorinated diphenyl No. 1	−25	7.10	2.76	4.3	5	0.27	16
	−30	(7.44)	2.76	3.6	4	0.31	16
		B: Solids					
Ice	−1	74	3.0	2.0	5	0.03	20
	−5	75	3.0	3.1	5	0.00	20
	−6	80	3.0	3.1	5	(0.08)	19
	−7.1	98	2.0	4.0	5	0.04	21
	−20	82	3.0	1.4	4	0.02	20
	−20	82	3.5	1.0	4	0.07	19
	−40	(81)	3.0	——		0.02	20
	−40	—	3.5	——		0.16	19
	−45.8	97	2.0	2.7	3	0.07	21
	−50	—	3.02	——		0.12	20
	−60	—	3.00	——		0.17	20
	−63.5	(117)	3.0	(1.6	2)	0.17	21
	−70	—	2.90	——		0.22	20
1,2,4-Trimethyl	−60	7.16	3.0	8.8	6	0.19	22
3,5,6-Trichlorobenzene	−80	7.85	3.0	8.4	5	0.31	22
Methylpentachlorobenzene	0	5.36	3.10	3.2	7	0.11	22
	−18	5.54	3.10	1.6	6	0.13	22
	−40	5.94	3.10	1.4	5	0.24	22
1,2,3,4-Tetramethyl 5,6-dichlorobenzene	−77	9.65	3.02	2.1	6	0.22	22
	−88	9.70	3.00	1.1	5	0.25	22
	−111	9.80	2.92	6.1	5	0.31	22
Pentamethylchlorobenzene	−61	7.34	2.94	5.9	6	0.18	22
	−70	8.00	3.00	1.8	5	0.21	22
	−79	8.60	2.92	5.0	5	0.26	22
Cyclopentanol	−70	48	4.3	7.6	6	0.12	23
Cyclohexanone	−130	20.9	3.3	1.6	8	0.55	23
Abietic acid	86.8	3.72	2.81	2.2	6	0.40	24
Chlorinated diphenyl No. 2	14	5.20	2.82	1.6	6	0.12	16
	5	5.49	2.82	2.8	5	0.20	16
	−1	(5.73)	2.82	——		0.28	16
Chlorinated diphenyl No. 3	37	4.06	2.80	3.5	6	0.13	16
	27.5	4.23	2.80	7.2	5	0.25	16
Plasticized polyvinyl chloride	25	(10.0)	3.04	1.3	4	0.61	32
Glycol phthalate resin	30	17.2	5.8	5.7	7	0.44	24
Phenol formaldehyde resin	70	8.25	3.40	1.1	5	0.60	33
Vinsol	98	8.48	3.42	1.2	4	0.61	24
Halowax	−40	6.70	3.40	4.8	7	0.42	15
	−50	6.75	3.40	2.4	6	0.54	15
	−60	6.80	3.40	3.5	5	0.64	15
Paraffin	21	—	—	——		(0.85)	27
Ceresin	21	—	—	——		(0.86)	27
Rubber, 20% sulphur	75	4.85	2.70	1.1	5	0.64	34
Rubber, 32% sulphur	135	5.70	2.70	5.3	5	0.68	34
Pyrex	21	—	—	——		(0.885)	27
Mica	21	—	—	——		(0.88)	27
Slate	?	(98)	8.0	2.7	4	0.53	24

* Values of ϵ_0, ϵ_∞, τ_0, α and the temperature of measurement are listed, together with the source of the data. Values which are doubtful because of inadequate frequency range or lack of consistency of the data are enclosed in parentheses. The values of α listed in such cases do not necessarily apply to the entire frequency range. The absence of an entry indicates that the data do not permit even an approximate estimate. The entries for τ_0 are given as values for a and b, respectively, in the equation $\tau_0 = a \cdot 10^{-b}$ sec.

∞ at right angles to the axis. If Eq. (5) is satisfied, the limiting slope of the locus is not infinite but rather $\tan\frac{1}{2}(1-\alpha)\pi$ as is evident from Fig. 2(b).

The latter behavior is found to be the general rule. An example is found in the data of Smyth and Hitchcock for ice at temperatures below −30°C as plotted in Fig. 5. As the temperature decreases, the limiting slopes show an increasing departure from the value of unity demanded by the Debye theory. At these lower temperatures it is clearly impossible to do more than guess at the nature of the dispersion except at the high frequency limit, and one can only suspect that, as in many other cases, the locus may well be a circular arc. It is still less possible to determine the value of the static dielectric constant, and one can only venture the opinion that it must be very large and attained only at extremely low frequencies.

MacLeod[27] has obtained data on several solid dielectrics which show the same characteristic. This observer determined the equivalent series resistance R_s and capacity C_s of glass, paraffin, ceresin wax, and mica over the frequency range 500c − 10^6c and found that the data could be represented by equations of the form $R_s = a\nu^{-k}$, $C_s = b(1+c\nu^{n-1})$. It is readily shown from Eqs. (7) that for $\omega\tau_0 \gg 1$ one obtains relations of this form and that $k = 2-\alpha$, $n = \alpha$. From this it is also seen that $n+k=2$, which MacLeod found to be the case to within 0.5 percent. These results are particularly interesting because they show that for these dielectrics a frequency of 500c is near the infinite frequency end of the dispersion range. Furthermore, the values of α lie between 0.85 and 0.90 so that the dispersion range is very wide and the static value of the dielectric constant is attained only at extremely low frequencies.

[27] H. J. MacLeod, Phys. Rev. **21**, 53 (1923).

B. Maximum value of the absorption

The second of Eqs. (7) predicts that the maximum value of ϵ'' for $\omega = 1/\tau_0$ is

$$\epsilon''_{\max} = \tfrac{1}{2}(\epsilon_0 - \epsilon_\infty)\tan[(1-\alpha)\pi/4]. \quad (9)$$

Data tabulated by Morgan[28] show that for a

[28] S. O. Morgan, J. Ind. and Eng. Chem. **30**, 273 (1938).

considerable number of alcohols, glycols, various chlorinated compounds, rosins and solids the value of ϵ''_{max} is considerably less than $\frac{1}{2}(\epsilon_0-\epsilon_\infty)$. This is, from Eq. (8), consistent with the circular arc locus and values of α greater than zero, although one is not, of course, entitled to deduce from these data alone that the dispersion is described by Eq. (5).

C. Dependence of the absorption conductivity on the frequency

Data in the literature on the "absorption conductivity"[29] of dielectrics as a function of frequency give further evidence consistent with Eqs. (7) for $\alpha>0$. This conductivity σ is from elementary considerations equal to $\epsilon''\omega$. At very low frequencies Eq. (7) gives

$$\epsilon=(\epsilon_0-\epsilon_\infty)(\omega\tau_0)^{2-\alpha}\cos\tfrac{1}{2}\alpha\pi. \qquad (10)$$

Thus, if $\omega\ll 1/\tau_0$, σ should be proportional to a power of ω between 1 and 2 for values of α between 1 and 0. An example of departures from the limiting square law frequency dependence is found in data of Dahms,[30] on aqueous sugar solutions. These experiments gave an absorption conductivity proportional to a power of ω between 1.88 and 1.56. From Eq. (9) these results correspond to values of between 0.12 and 0.44.

Schmale,[31] has measured σ for water, nitrobenzol, chlorobenzol, and acetone for wavelengths from 10 m to 20 m. He found that the absorption conductivity was proportional to ω^2 in all cases, in agreement with the Debye theory. Because of the rather limited frequency range and the discrepancies between data of Bäz and Slevogt on polar liquids, this evidence cannot be regarded as conclusive.

It is clear from the examples which have been discussed in this section that the circular arc locus and the equivalent analytic representation of Eq. (5) are an excellent description of the dispersion in a large number of dielectrics. This description requires the introduction of the single parameter α in addition to the constants ϵ_0, ϵ_∞, τ_0. The experimental results are thus completely described by these four quantities and the values found for the examples considered in the present work are listed in Table I.[32-34]

VI. Proposed Modifications of the Simple Dispersion Theories

The fact that a considerable amount of experimental data can be represented by Eq. (5) with $\alpha>0$ does not of course explain why this kind of result should occur. It has long been recognized that the Debye Eqs. (1) are not valid in many cases, and various explanations have been put forward to account for the observed deviations. The fact that so many of these deviations are represented analytically by Eq. (5), graphically by the circular arc locus, or electrically by a complex impedance with phase angle independent of the frequency has not previously been brought out.[35] It is therefore of importance to examine whether this characteristic behavior is accounted for by any of the proposed explanations.

A. Hindered rotation

The hypothesis of hindered rotation has been applied to the problem of the static dielectric constant of polar liquids by Debye,[36] and to dispersion in polar liquids by Debye and Ramm.[37] The difficulties with the concept in the two cases have been discussed elsewhere.[38] For the sake of completeness, the relation of the theory of Debye and Ramm to the experimental results on dispersion will be outlined briefly.

If the effect of the assumed hindered rotation is small, the term $1/(1+i\omega\tau_0)$ in Eq. (1) is replaced by a series of the form

$$\sum \frac{c_n}{1+i\omega\tau_0/\lambda_n}, \qquad (11)$$

and the frequency dependence of ϵ^* is modified.

[29] It should be emphasized that this "absorption conductivity" refers only to the conductivity associated with dispersion. It does not include any "direct current" steady-state conductivity as will be discussed in a later paper (reference 6).

[30] W. Dahms, Physik. Zeits. **37**, 158 (1936). See also: M. Wien, Physik. Zeits. **37**, 870 (1936).

[31] K. Schmale, Ann. d. Physik **35**, 671 (1939).

[32] W. A. Yager, Trans. Electrochem. Soc. **74** (preprint) (1938).

[33] L. Hartshorn, N. J. L. Megson, and E. Rushton, Proc. Phys. Soc. **52**, 796 (1940).

[34] A. H. Scott, A. T. McPherson, and H. L. Curtis, Bur. Stand. J. Research **11**, 173 (1933).

[35] See, however, reference 10.

[36] P. Debye, Physik. Zeits. **36**, 100, 193 (1935).

[37] P. Debye and W. Ramm, Ann. d. Physik **28**, 28 (1937).

[38] See, for instance, J. H. Van Vleck, J. Chem. Phys. **5**, 556 (1937), and reference 3.

The experimental deviations from Eq. (1), for polar liquids, however, occur in strongly polar liquids for which the theory predicts only a single dispersion term of the form (10). Furthermore, the departures increase with decreasing temperature, a behavior which is again contrary to the theory.

The series (11) cannot in any case reasonably be expected to account for Eq. (5). The nature of the difficulty is readily seen by considering the expression (7) for ϵ''. This expression is logarithmically symmetrical in the frequency about the value $\omega=1/\tau_0$. The series (11) must then give this same characteristic symmetry which can be the case only if the constants c_n have the same value for $\lambda_n=1/n$ as for $\lambda_n=n$. It is difficult to see any reason for such a symmetrical distribution of the c_n. Furthermore, this distribution must be a very broad one to account for values of α much greater than zero (cf. under **C**). In addition, the distribution must approximate a continuous one as otherwise the limiting behavior at very low or very high frequencies will be given essentially by a single term of the series. This would require limiting 90° angles of approach to the ϵ' axis of the complex plane locus. As is evident from the discussion in III and V, this behavior is not found experimentally.

B. Effect of molecular shape

In the original Debye treatment for polar molecules the molecules are assumed to be spherical. If a more general assumption of an ellipsoidal form is made, one obtains instead of a single relaxation time three related in terms of the axial ratios of the ellipsoid.[39] A series of the form (11) with three terms is then obtained. The difficulties with this hypothesis as a general explanation are then covered in the discussion under **A**.

C. Distribution of relaxation times

The concept of a distribution of relaxation times was first introduced by von Schweidler.[40] Later Wagner[5] proposed the use of a logarithmic Gaussian distribution of the form

$$F(s)ds=(b/\pi^{\frac{1}{2}})\exp(-b^2s^2)ds, \qquad (12)$$

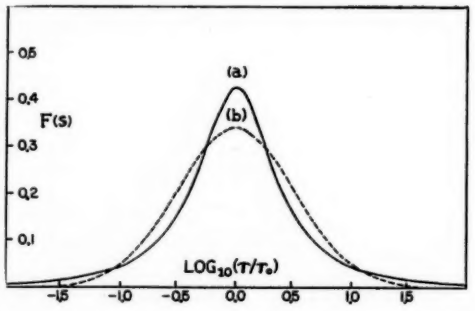


FIG. 9. Distribution of relaxation times $F(s)$, where $s=\log_e(\tau/\tau_0)$; (a) calculated from circular arc locus for $\alpha=0.23$, (b) logarithmic Gaussian distribution for $b=0.6$.

where $s=\log_e(\tau/\tau_0)$ and b determines the breadth of the distribution. As Fuoss and Kirkwood[41] have shown, it is possible to calculate the distribution necessary to account for any given experimental results from the observed ϵ''—frequency relation. If the general relation (7) for ϵ'' is used, their analysis is easily shown to give the result

$$F(s)ds=\frac{1}{2\pi}\cdot\frac{\sin\alpha\pi}{\cosh(1-\alpha)s-\cos\alpha\pi}ds. \qquad (13)$$

It is interesting to compare this result with Eq. (12). Yager[24] has evaluated ϵ' and ϵ'' from Eq. (12) by numerical integration and from his values it is possible to find the value of b which corresponds most closely to a given α. As an example the two distributions for $b=0.6$ and the corresponding value 0.23 of α are plotted in Fig. 9. It is evident that the Gaussian distribution (dashed curve) requires too great a concentration of relaxation times for values of τ which are comparatively close to τ_0 and that the distribution (13) is considerably broader. The necessary breadth increases rapidly for larger values of α and the Gaussian distribution (12) is an increasingly poorer approximation. For $\alpha=0.5$, 95 percent of the relaxation times are included in the range $0.001<\tau/\tau_0<1000$, while for $\alpha=0.75$ only 72 percent are included in the same range.

Although the distribution (13) is formally an exact representation of the circular arc locus and Eq. (5), there remains the difficulty of accounting for such a broad distribution as is required in many cases. An even greater difficulty is en-

[39] J. Perrin, J. de phys. et rad. [7]5, 497 (1934); A. Budo, Physik. Zeits. **40**, 603 (1939).
[40] E. von Schweidler, Ann. d. Physik **24**, 711 (1907).
[41] R. Fuoss and J. G. Kirkwood, J. Am. Chem. Soc. **63**, 385 (1941).

countered in attempting to account for the essential logarithmic symmetry of this distribution. In the absence of any satisfactory explanation of these features, the distribution function is nothing more than a means of expressing the experimental results which is equivalent to the circular arc locus or Eq. (5).

D. Complex coefficient of viscosity

Gemant[42] has suggested that, by analogy with observed elastic effects in solid friction, one might expect in the case of polar dielectrics a complex coefficient of viscosity or solid friction in the relaxation time of Eq. (1). This viscosity η^* must be of the form

$$\eta^* = \eta_0 (i\omega)^{-\alpha},$$

η_0 being a constant, if Eq. (5) is to result.

An assumption of this kind does not, of course, explain the experimental results but merely restates the problem in terms of a concept which itself remains to be explained. There is therefore little to be gained by this approach.

E. Other suggested modifications

Gemant has also proposed that the dispersion term $1/(1+i\omega\tau_0)$ in Eq. (1) be replaced by an expression of the form $[1-(i\omega\tau_0)^g]/[1-(i\omega\tau_0)^h]$, where $g=(4j\pm1)/(4k\pm1)$, $h=(4l+2)/(2m+1)$, with j, k, l, m integers. This expression reduces properly to $1/[1+(i\omega\tau_0)^{1-\alpha}]$ only if $g=\frac{1}{2}h=1-\alpha$. In the absence of a fundamental basis for the suggested expression, this procedure offers nothing in the way of explanation for Eq. (5).

Other modifications of the simple dispersion theories which have been suggested either have no effect on the frequency dependence or are incapable of accounting for the particular type of dispersion found experimentally as expressed by Eq. (5).

[42] A. Gemant, Physics **7**, 311 (1936).

VII. Conclusion

The experimental data which have been discussed are believed to be representative of a considerable number and variety of dielectrics. There is no doubt that dispersion and absorption in these dielectrics may be due to one or more of several types of polarization. The remarkable fact is that the experimental results are so generally expressed by an empirical formula involving a single new constant α.

The hypothesis of a distribution of relaxation times, although a natural one to consider, leads to a general distribution formula with the one disposable parameter α. Both the breadth and form of this distribution are difficult to understand. The fact that so many otherwise dissimilar dielectrics exhibit the same characteristic form of dispersion suggests that a more general fundamental mechanism or process must be involved.

The ordinary mechanisms proposed to explain dielectric absorption (e.g., viscous damping, direct current conductivity) have the common feature that they are purely dissipative in character. This is represented in the equivalent circuit of the dielectric by a pure resistance. The actual behavior of dielectrics, however, requires that the dispersion mechanism be equivalent to a complex impedance as shown in Fig. 2 (b). It therefore implies a conservation or "storage" of energy in addition to dissipation of energy in the mechanism of molecular interaction responsible for the dispersion. The characteristic feature of the equivalent complex impedance, a phase angle which is independent of frequency, has a very simple statement in terms of energy. Namely, the ratio of the average energy stored to the energy dissipated *per cycle* in the form of heat is a constant independent of the frequency. The simplicity of this result suggests that the problem may profitably be considered from this viewpoint.

The Measurement of the Dielectric Constants of Vapors and the Polarizations of Trimethylaluminum, Dimethylaluminum Chloride and Methylaluminum Dichloride

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Modifications of an apparatus for the measurement of the dielectric constants of vapors are described. The apparatus has been used to determine the dielectric constants of the vapors of trimethylaluminum and dimethylaluminum chloride over a range of temperature and pressure, and methylaluminum dichloride has been measured in solution with another apparatus. The accurate calculation of the dipole moments of the molecules is prevented by strong molecular association. The data indicate a strong probability that the single trimethylaluminum molecule has a pyramidal structure and that the aluminum-carbon bond is predominantly covalent.

THE dipole moments of trimethylaluminum, dimethylaluminum chloride and methylaluminum dichloride would be of considerable interest not only because of the light which they might throw upon the molecular structures of these compounds but also as a means of obtaining moment values for the aluminum bonds for examination in connection with the electronegativity of aluminum. Dr. George Calingaert of the Ethyl Gasoline Corporation has made an investigation of these substances possible by providing several small bulbs containing weighed quantities of the compounds, which were thus handled without exposure to air. Because of the tendency of the methylaluminum dichloride to decompose, it was thought safer to measure it at 25° in benzene solutions, which were made up by breaking the bulbs under weighed quantities of benzene. These solution measurements were carried out by Mr. P. F. Oesper.

APPARATUS AND METHOD

For the gas measurements, the bulbs were broken by a magnetic breaker after having been sealed in the apparatus, which was evacuated before the bulb was broken. In order to save material, a capillary U-tube was used instead of the usual larger U-tube filled with the liquid in question to separate the vapor in the measuring cell from the nitrogen filling the rest of the apparatus and measure any pressure difference between them. The apparatus used for the measurement of the dielectric constants of the vapors was a heterodyne-beat apparatus which had evolved gradually from the one employed for a large number of measurements some years ago.[1] The electrical circuits had been altered extensively and the large shielding box enclosing them had been thermostated so that the circuits and the precision and reference condensers could be kept at a temperature constant[2] within 0.2°. The stability of the circuits was increased by replacement of old fixed mica condensers by instruments of better quality.

In all the earlier measurements, the sensitivity of the capacity measurements was magnified by connecting the precision condenser on which the readings were made in series with a small fixed mica condenser. Large constant errors discovered in calibration measurements when the apparatus was used after long periods of idleness were attributed to the use of this series arrangement. It was, therefore, replaced by a single condenser of large scale and capacity so small that it could be used for compensating accurately the very small change in the capacity of the measuring condenser produced by changing the pressure of the gas in it. A condenser was constructed for this purpose by removing the plates from an old General Radio Company Type 722 1500 $\mu\mu$f precision condenser, replacing the set of semicircular, movable plates by a single aluminum plate of much reduced size, and restoring two of the fixed plates so that the movable plate could turn between them, the plate separation being greater

[1] K. B. McAlpine and C. P. Smyth, J. Am. Chem. Soc. **55**, 453 (1933).
[2] J. M. A. deBruyne and C. P. Smyth, J. Am. Chem. Soc. **57**, 1203 (1935).

than before. The total variable capacity of the condenser was now only about 7 $\mu\mu$f and its variation was covered by a scale of 2500 divisions which could be estimated to 0.1 division. The actual sensitivity of the setting was 0.2 scale division.

The condenser was calibrated by a modification of the usual method.[3] The arbitrary fixed capacity unit in terms of which it was to be calibrated had to be very small. This small capacity unit was obtained by mounting in parallel with the condenser to be calibrated, already in its final position in the apparatus, a General Radio Company type 722 D precision condenser, to the screw of which a long glass tube was attached and extended through the top of the shielding box. This tube was bent through a right angle just above the top of the box to form a lever. The turning of the lever was restricted to a small angle by two nails driven into the top of the box. When it was turned against one nail, the capacity of the precision condenser was increased. When it was turned from this nail back to the other, the capacity was decreased by a fixed amount, about 0.06 $\mu\mu$f, which formed the unit of calibration of the low capacity precision condenser. This unit could thus be alternately added or subtracted without any change in contacts or leads.

Experimental Results

It has been customary in using this apparatus to make measurements over a range of pressure down to about 20 mm, and to plot the capacity against the pressure. The curves thus obtained are straight lines at the lower pressures, but show very slight curvature at the higher pressures, where deviations from the ideal gas law cause a very slight increase in the number of molecules per unit volume above the number given by the ideal gas law and a corresponding slight increase in the capacity or dielectric constant. The curves thus obtained for trimethylaluminum and dimethylaluminum chloride at several temperatures were typical of those obtained for normal, unassociated vapors, although the experimental errors were somewhat larger than usual because of the instability of the substances, which prevented the use of high temperatures and an extended pressure range. The dielectric constants ϵ calculated from the linear portions of these capacity-pressure curves were used to calculate the polarizations, $P=22414T(\epsilon-1)/273.1(\epsilon+2)$, T being the absolute temperature. The values thus obtained are given in the second column of Table I. Because of the rapidity of decomposition of these substances in contact with air, their refractive indices were not measured. Their molar refractions, however, were calculated from the refractions of aluminum chloride and aluminum bromide measured by Bredig and Koch[4] and the atomic refractions given in Landolt-Börnstein. The apparent dipole moment μ calculated from the difference between each polarization value and the refraction, 22.9 for trimethylaluminum and 23.1 for dimethylaluminum chloride is given in the third column of Table I. At the bottom of the table are the polarization values of methylaluminum dichloride calculated on the assumption that it is monomeric from the dielectric constants and densities of solutions in heptane containing mole fraction c_2 of solute. The moment is calculated from the difference between the polarization value 103 obtained by extrapolating the P_2-c_2 curve to $c_2=0$ and an estimated refraction 23.

These apparent moment values are quite consistent with one another, for one would expect the moment associated with the Al−Cl bond to be

Table I. *Apparent polarization and dipole moment values (molecular association disregarded).*

T°K	P	$\mu(\times 10^{18})$
	Trimethylaluminum	
360.1	57.6	1.43
384.1	56.7	1.46
398.0	50.4	1.34
	Dimethylaluminum chloride	
324.8	73.1	1.63
348.1	68.5	1.61
371.1	67.6	1.65
395.3	66.7	1.69
416.4	66.7	1.73
	Methylaluminum dichloride ($T=298.1$°K)	
c_2		
0.000000	103	1.96
.006209	90.5	
.006683	87.9	
.014799	73.7	

[3] C. P. Smyth, *Dielectric Constant and Molecular Structure* (The Chemical Catalog Company, New York, 1931), p. 52.

[4] M. A. Bredig and F. K. V. Koch, Zeits. f. physik. Chemie **B24**, 187 (1934).

considerably larger than that of the Al−C bond, so that each replacement of a methyl group by a chlorine atom should increase the moment, as it does. However, the results of vapor density measurements presented by Dr. A. W. Laubengayer of Cornell University at the Detroit meeting of the American Chemical Society and very kindly communicated by him to the authors indicate that trimethylaluminum exists largely as a dimer $[(CH_3)_3Al]_2$ in the region of temperature and pressure employed in the present measurements. The aluminum halides also are known[5] to exist as dimeric molecules in the vapor state below 400°C. It is, therefore, desirable to examine the polarization values calculated at each pressure and temperature for evidence of molecular association and of its effect upon the moment values. These polarization values at pressure p are listed in Table II in the order in which they were measured at each temperature with the object of showing whether appreciable decomposition of the material occurred during the course of the measurements.

TABLE II. *Dependence of polarization upon pressure and temperature.*

p(MM)	P	p(MM)	P
Trimethylaluminum			
$T=360.1$°K		$T=398.0$°K	
27.8	58.0	20.0	50.0
46.8	57.5	55.0	52.5
66.7	57.5	76.8	50.1
58.4	57.9	100.6	49.6
36.2	60.0	123.1	50.4
$T=384.0$°K		160.6	54.5
22.3	65.6		
46.9	60.9		
103.0	56.0		
75.9	54.6		
124.9	56.4		
154	57.7		
Dimethylaluminum chloride			
$T=324.8$°K		$T=395.3$°K	
13.6	71.7	31.3	66.8
38.4	72.3	65.5	66.3
49.8	74.9	91.0	67.1
28.0	74.0	132.5	66.2
$T=348.1$°K		166.4	66.8
16.9	74.6	189.3	67.2
39.5	68.2	$T=416.4$°K	
83.4	68.9	36.1	65.5
99.9	69.1	63.2	66.8
126.1	72.5	107.5	66.6
$T=371.1$°K		141.7	66.0
10.0	(74.3)	179.9	66.9
53.2	65.7	209.5	67.0
91.7	65.9		
132.1	65.9		
173.6	66.5		
195.3	67.2		

DISCUSSION OF RESULTS

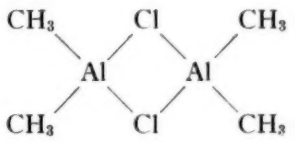
The polarization values in Table II show no regular dependence upon pressure such as might be expected to arise from a pressure-dependent equilibrium between a monomer and a dimer, nor is there any appreciable drift with time to give evidence of chemical change. In order to analyze the effect of molecular association upon the apparent values of the polarization, the values of the equilibrium constant K for the dissociation of the dimer, $(CH_3)_6Al_2$, were calculated for the temperatures here used by plotting log K for the values of K given us by Dr. Laubengayer against $1/T$ and interpolating. The degree of dissociation α was then calculated at each pressure p as $\alpha=[K/(4p+K)]^{\frac{1}{2}}$. The observed polarization P may be regarded as a combination of the polarization P_1 of the dimer and P_2 of the monomer and written $P=c_1P_1+c_2P_2$, where c_1 and c_2 are the respective mole fractions. As $c_1=(1-\alpha)/(1+\alpha)$ and $c_2=2\alpha/(1+\alpha)$, substitution and rearrangement gives $P_2=1/2[(P-P_1)/\alpha+(P+P_1)]$. The values of P_2 were calculated at each pressure and temperature by assigning to the dimer the polarization value $P_1=46$, arrived at by assuming the dimer to be a symmetrical structure with zero moment and polarization consequently equal approximately to its molar refraction, which should be approximately double that for the monomer, 23. The values of P_2 calculated by the above expression have probable errors of, at least, 10 percent, because of the division of the small difference $P-P_1$ by the small values of α, and show a tendency to be larger the smaller the value of α, instead of being practically independent of pressure as they should be. This behavior naturally follows from the fact that the observed values of P are almost independent of pressure. Moreover, as the degree of dissociation increases with rising temperature, the values of P_2 fall off more rapidly than they should according to the Debye equation. Consequently, the moment values calculated from them decrease with rising temperature, the values being about 2.4×10^{-18} at 360.1°K, 2.2 at 384.1°, and

[5] See K. J. Palmer and N. Elliott, J. Am. Chem. Soc. **60**, 1852 (1938).

1.6 at 398.0°. As there is a distinct possibility that the molar refraction of the dimer may be a little higher than 46, and the atomic polarization should raise it a little more, the calculations were repeated with a value of 50 for P_1. The average moment value at each temperature was thereby reduced by about 0.3×10^{-18}. By using a value $P_1=61$, the moment value was reduced approximately to zero at 398°, but was still considerable at the two lower temperatures. However, 50 is close to the upper limit of the value which can reasonably be assigned to P_1, the polarization of the dimer, unless its molecule has an altogether abnormal atomic polarization or a small permanent moment because of an unsymmetrical structure. As there is more of the monomer present at the highest temperature, more weight should, probably, be given to the moment value found there. The logical conclusion to be drawn from these results is that the monomer $(CH_3)_3Al$ has a moment value $1.6\pm0.8\times10^{-18}$, which is close to the value obtained when all association is neglected. It must, however, be borne in mind that the curious behavior which has been described, possibly the result of an unsuspected amount of decomposition, and the remote possibility of an abnormally high atomic polarization leave an element of doubt as to the validity of the conclusion.

Because data are not available as to the association of dimethylaluminum chloride and methylaluminum dichloride, which, in view of the association of trimethylaluminum and the aluminum halides, should be strongly associated, moment values cannot be obtained for their monomeric forms. It can, however, be concluded that the molecules possess considerable moments as indicated by the apparent values in Table I.

In view of the fact that trimethylboron and boron trichloride have symmetrical planar structures,[6] one would anticipate a similar structure for trimethylaluminum, which, of course, would have zero dipole moment. However, there is a pronounced difference between the two boron compounds and the corresponding aluminum compounds in that the former exist as monomers while the latter exist largely as dimers. The results of electron diffraction have been interpreted[5] as showing the two aluminum atoms of the dimeric aluminum halides to be held together by two halogen atoms shared in common between them, each aluminum being at the center of a distorted tetrahedron with a halogen atom at each of the four corners of the tetrahedron, one edge of which is shared with the other tetrahedron. If this structure is correct for the aluminum halides, one would expect double molecules of dimethylaluminum chloride and methylaluminum dichloride to form through the holding of two halogen atoms in common between two aluminum atoms. The dimeric form of the dimethylaluminum chloride,



would then have zero moment, while the monomeric form would have a moment dependent upon the difference between the Al−Cl and the Al−C bond moments, which should be considerable. The dimer of methylaluminum dichloride should exist in a *cis*-form having a considerable moment and a *trans*-form having zero moment, while the monomeric molecule with two Al−Cl bond moments should have a moment considerably larger than that of the monomeric molecule of dimethylaluminum chloride.

The trimethylaluminum molecule contains nothing to form a link between two aluminum atoms but the orbitals of the aluminum atoms. One must, therefore, ascribe to the dimer a more or less ethane-like structure with the two aluminum atoms directly bonded to each other. In view of this bonding here, one may wonder if there may not be a strong possibility of direct aluminum-aluminum bonding in the dimeric molecules of the halogenated aluminum compounds. Since there is evidently a marked difference between the behavior of the boron and the aluminum compounds, it is not unreasonable to suppose that a difference may exist between the structures of the $(CH_3)_3B$ and the $(CH_3)_3Al$ molecules. The sp^2 configuration which one would naturally ascribe to the boron and aluminum orbitals in these molecules has been shown by

[6] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, second edition, 1940), p. 88, 233.

Pauling[7] to give rise to a trigonal plane structure, a pyramidal structure also being possible but less stable because of repulsive forces.[8] The larger size of the aluminum atom would make these repulsive forces less in the $(CH_3)_3Al$ than in the $(CH_3)_3B$ molecule, thereby increasing the stability of a possible pyramidal structure. If the pyramidal structure gave the tetrahedral angle 110° to the C−Al−C valence angle, the Al−CH_3 moment would be the same as that roughly calculated for the molecule, 1.6×10^{-18}, and the Al−C bond moment, which presumably acts in the opposite direction to the H−C moment, would be 1.6 increased by the estimated value 0.3 of the H−C moment, or 1.9×10^{-18}. Reduction in the size of the C−Al−C valence angle reduces the value calculated for the Al−C moment. If the C−Al−C angle is 90°, the value calculated for the Al−C bond moment is 1.2×10^{-18}, while if the angle is greater than 110°, the Al−C bond moment is greater than 1.9×10^{-18}. These very rough values estimated for the Al−C bond moment are considerably smaller than one would expect for the aluminum-halogen bond moments and are consistent with the small magnitude of moment and predominantly covalent character attributed to metal-carbon bonds.[9]

Because of the considerable importance of the structures of aluminum compounds, it has seemed desirable to present these experimental data in spite of the difficulties which molecular association introduces into their interpretation. Although these difficulties are such as to render any conclusions somewhat uncertain, the data do indicate a strong probability that the monomeric trimethylaluminum molecule has a pyramidal structure and that the aluminum-carbon bond is largely covalent.

[7] Pauling, J. Am. Chem. Soc. **53**, 1367 (1931).
[8] G. E. Kimball, J. Chem. Phys. **8**, 188 (1940).
[9] G. L. Lewis, P. F. Oesper and C. P. Smyth, J. Am. Chem. Soc. **62**, 3243 (1940).

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Induction and Dipole Moment in Chloro- and Nitroparaffins

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The dielectric constants of the vapors of the butyl chlorides, methyl chloroform, nitromethane, α- and β-nitropropane, and 2-methyl-2-nitropropane have been measured over a range of temperature and pressure and used to calculate the dipole moments of the molecules of these substances. The dipole moment increases from normal to secondary to tertiary butyl chloride much less than indicated by the apparent moments previously measured in solution, it being shown that the apparent solution values for the primary and secondary compounds are lowered by solvent effect. The moments found for α- and β-nitropropane and 2-methyl-2-nitropropane are indistinguishable from one another, but are slightly larger than that of nitromethane. Examination of the molecular models shows that the moment differences found are approximately those to be expected from the inductive effects, with the exception of the large difference between chloroform and methyl chloroform where it can only be said that induction is a major cause of the difference.

INDUCTION is often such an important factor in the interpretation of dipole moment data that it has seemed desirable to check up on certain ideas as to induction effects which were originally based upon moment values determined in solution and thus subject to the uncertainties introduced by solvent effects. This checking up process has been carried out by measuring the dipole moments in the vapor state of the four butyl chlorides and methyl chloroform previously measured in solution and of four nitroparaffins, two of which had previously been measured as vapors. The measurements were carried out with the modified heterodyne beat apparatus previously described,[1-3] the

[1] K. B. McAlpine and C. P. Smyth, J. Am. Chem. Soc. **55**, 453 (1933).
[2] J. M. A. de Bruyne and C. P. Smyth, J. Am. Chem. Soc. **57**, 1203 (1935).
[3] R. H. Wiswall and C. P. Smyth, J. Chem. Phys. **9**, 352 (1941).

dielectric constant being determined at each temperature over a wide range of pressure so as to eliminate the effects of deviations from the ideal gas law. Air and *n*-butyl chloride were used in calibrating the apparatus, the capacity of the gas-containing condenser being determined finally from measurements on the *n*-butyl chloride vapor, which had been accurately determined previously.[4]

Purification of Materials

The chloroparaffins, obtained from the Eastman Kodak Company, were purified by thorough washing with water or sulfuric acid followed by sodium carbonate solution, drying over calcium chloride, and fractional distillation. The *i*-butyl chloride was purified by Dr. Anthony Turkevich in this laboratory. The nitromethane was part of an old sample from the Eastman Kodak Company, and the two nitropropanes were very kindly given us by the Commercial Solvents Corporation. These substances were dried over calcium chloride and fractionally distilled. The 2-methyl-2-nitropropane was given us by Professor R. H. Ewell of Purdue University. It was used without further purification. The boiling points and refractive indices for the sodium *D* line at 20° determined for the compounds as criteria of purity are given in Table I, which also lists the molar refractions, MR_D.

Experimental Data

The polarizations *P* calculated from capacity-pressure curves at each absolute temperature *T* are listed in Table II. As the tendency of some

Table I. *Boiling points, refractive indices, and molar refractions.*

	B.p., °C	n^{20}_D	MR_D
n-C_4H_9Cl	78	1.4023	25.5
i-C_4H_9Cl	68.2	1.3983	25.4
s-C_4H_9Cl	68.1	1.3969	25.7
t-C_4H_9Cl 1st sample	50.6	1.3853	
2nd sample	50.8 (756 mm)	1.3858	25.9
CH_3CCl_3	74.5 (767 mm)	1.4384	26.1
CH_3NO_2	101.0	1.3824	12.5
n-$C_3H_7NO_2$	130.9 (753 mm)	1.4003	21.6
i-$C_3H_7NO_2$	120.1 (763 mm)	1.3949	21.6
t-$C_4H_9NO_2$	122–124	1.4015	26.1

[4] C. P. Smyth and K. B. McAlpine, J. Chem. Phys. **3**, 347 (1935).

Table II. *Polarizations and dipole moments.*

		Moment ($\times 10^{18}$)	
T, °K	P	(Using MR_D)	(Using P_E+P_A)
	i-Butyl chloride		
345.2	99.1	2.05	2.00
360.0	95.7	2.04	2.00
368.0	93.9	2.04	1.99
387.5	92.0	2.06	2.01
406.5	87.8	2.04	1.99
	Mean value = 2.04		2.00
	s-Butyl chloride		
335.9	106.3	2.11	2.07
351.9	102.6	2.11	2.07
371.2	99.6	2.12	2.08
392.0	95.3	2.12	2.08
	Mean value = 2.12		2.08
	t-Butyl chloride 1st sample		
314.1	114.1	2.13	2.10
339.7	104.6	2.10	2.06
	t-Butyl chloride 2nd sample		
324.3	111.1	2.13	2.10
340.8	108.1	2.15	2.11
341.9	109.4	2.17	2.13
354.1	101.4	2.10	2.06
	Mean value = 2.13		2.09
	Methyl chloroform		
335.8	83.9	1.79	
347.7	81.5	1.78	
372.0	77.4	1.77	
398.6	73.1	1.75	
	Mean value = 1.77		
	Nitromethane		
367.8	215.4		
421.0	190.9		
	α-Nitropropane		
382.0	242.5	3.73	3.68
406.4	230.5	3.74	3.68
408.9	227.7	3.72	3.67
421.2	223.8	3.74	3.69
438.0	210.8	3.69	3.64
457.0	204.4	3.71	3.65
	Mean value = 3.72		3.67
	β-Nitropropane		
391.8	237.4	3.73	3.68
406.9	231.8	3.75	3.70
422.0	218.4	3.71	3.64
439.0	213.3	3.72	3.66
454.9	208.3	3.74	3.68
	Mean value = 3.73		3.67
	2-Methyl-2-nitropropane		
379.1	246.9	3.71	3.66
398.9	238.9	3.74	3.69
416.4	227.7	3.72	3.66
432.5	219.5	3.71	3.65
449.3	210.8	3.69	3.64
	Mean value = 3.71		3.66

of the compounds to decompose at high temperatures limited the range of temperature over which the measurements could be made, the dipole moment μ was calculated at each temperature from the difference between P and MR_D. As an atomic polarization $P_A=3.8$ had been found for n-butyl chloride,[4] values were also calculated for the moments of the butyl chlorides by using, instead of MR_D, the total induced polarization $P_E+P_A=28.5$ previously found for n-butyl chloride and similar induced polarization values calculated for the nitroparaffins by using the atomic polarization value 6.1 previously found for nitromethane.[5] The two slightly differing sets of moment values are listed for comparison in Table II, the mean value being listed at the bottom of each column. The true value for each substance presumably lies between these two mean values, but should not, in any event, be higher than the value calculated by the use of MR_D by more than the probable experimental error 0.02×10^{-18}. The values calculated by the use of MR_D are, therefore, adopted as correct and used in Table III for comparison with other values determined in this laboratory and elsewhere and taken from the literature. Only two values of the polarization are given for nitromethane as they were redetermined merely as a check. The values interpolated for these temperatures from the data of Smyth and McAlpine[5] are 215.0 and 190.2, in excellent agreement with the values obtained here.

Discussion of Results

As we are primarily concerned with the interpretation of small differences among the observed dipole moments, it is desirable to compare their accuracy with that of measurements on alkyl halides previously made in this laboratory[6] and with that of determinations of Groves and Sugden[7] upon several homologous series. These values are collected in Table III for comparison as well as interpretation, the values determined by Smyth and McAlpine being followed by an M, those of Groves and Sugden by a G and those obtained in the present investigations and reported in Table II being left unmarked.

Table III. *Moments* ($\times10^{18}$) *of homologous series in the vapor state.*

	F	Cl	Br	I	NO_2
CH_3	1.81M	1.87G	1.78M 1.79G	1.59M 1.64G	3.50M 3.54G
C_2H_5	1.92M	2.05G	2.02M 2.01G	1.90M 1.87G	3.58G
n-C_3H_7		2.10G	2.15G	2.01G	3.57G 3.72
n-C_4H_9		2.11G 2.09M	2.15G	2.08G	3.55G
n-C_5H_{11}		2.12G			
n-C_7H_{15}			2.15M		
i-C_3H_7		2.15G	2.19G		3.73
i-C_4H_9		2.04			
s-C_4H_9		2.12	2.20G		
t-C_4H_9		2.13			3.71

The values of Groves and Sugden for methyl, ethyl, and n-propyl chloride were recalculated from the measurements of other investigators on the assumption, employed in calculating from their own experimental data, that $P_E+P_A=1.05MR_D$. The values of Smyth and McAlpine were obtained from the slopes of the $P-1/T$ curves, except for the n-butyl chloride and n-heptyl bromide values, which were obtained from the difference $P-MR_D$. The n-butyl chloride value was originally obtained from the $P-1/T$ curve as 2.04, but the P_A value given by this curve was sufficient to lower it appreciably in comparison to values calculated by the other method. The higher value obtained from $P-MR_D$ is, therefore, given in Table III for comparison with that obtained by Groves and Sugden from $P-1.05MR_D$. The values of P_A obtained by Smyth and McAlpine for the methyl and ethyl halides are so near to the allowances for this quantity made by Groves and Sugden that no discrepancy between the two sets of values can arise from this source. It is evident from the calculations of moment in two ways in Table II that Groves and Sugden's method of subtracting $1.05MR_D$ instead of MR_D from the polarization would lower the moment by only 0.01 or 0.02×10^{-18} below the value obtained by subtracting MR_D. The probable error given by Groves and Sugden for their results is 0.01×10^{-18}, but as they have sometimes taken as the correct value a mean of their value and others in the

[5] C. P. Smyth and K. B. McAlpine, J. Am. Chem. Soc. **56**, 1697 (1934).
[6] C. P. Smyth and K. B. McAlpine, J. Chem. Phys. **2**, 499 (1934).
[7] L. G. Groves and S. Sugden, J. Chem. Soc. 158 (1937).

literature giving a result 0.02 different from theirs, and as their several values for a substance show much the same variation as those in Table II, their probable error may be taken to be the same as that in the results of Table II. It would not, therefore, be surprising to encounter occasionally a difference between values for the same substance as great as 0.04, which might be increased by 0.01 or 0.02 by use of $1.05MR_D$ instead MR_D. In order to make the values in Table III a direct comparison of three consistent sets of measurements, the values quoted from the paper of Groves and Sugden are those calculated wholly from their own measurements rather than the occasionally slightly different mean values which they estimated from their own and literature values. The greatest difference between the value of Groves and Sugden for any of the five alkyl halides previously measured by Smyth and McAlpine and that found by the latter is seen to be 0.05 and the average difference is only 0.02. There is, however, a noticeable discrepancy among the values for the nitroparaffins. The value found in the present investigation for α-nitropropane, which is indistinguishable from those found for β-nitropropane and 2-methyl-2-nitropropane, is 0.15 higher than the value found by Groves and Sugden for this compound, which, in their measurements, is very close to the values found for nitromethane, nitroethane and α-nitrobutane. Because of this discrepancy, a few measurements were made upon nitromethane, the close agreement previously noted being obtained with the results of Smyth and McAlpine,[5] which, when calculated with MR_D instead of the larger value of P_E+P_A containing $P_A=6.1$, give a value only 0.04 lower than that of Groves and Sugden. The good agreement between the boiling point, 130.9° at 753 mm, of the α-nitropropane used in the present investigation and the boiling point, 131.4° at 766 mm, of the material used by Groves and Sugden provides evidence against impurity as the source of the discrepancy.

The increases in moment of the alkyl halides and some other alkyl compounds on going from the methyl to the ethyl compound and of the solution values for the butyl halide moments on going from primary to secondary to tertiary have been attributed to dipoles induced by the carbon-halogen dipole in the groups immediately attached to the primary carbon.[8] As is evident in Table III, the methyl-ethyl moment difference increases by about 0.07×10^{-18} for each change from fluorine to chlorine to bromine to iodine. The smaller increase from the ethyl to the *n*-propyl halides, which was not evident in the earlier values for the chlorides, also increases by about the same amount on the change from chlorine to bromine, which is about the same as that from bromine to iodine. Any increase in moment on going from the *n*-propyl to the *n*-butyl halides is too small to be evident except in the case of the iodide, where the difference is again 0.07×10^{-18}. The long *n*-heptyl bromide molecule has the same moment as the *n*-butyl and *n*-propyl bromide molecules. Groves and Sugden[7] explained qualitatively the change in the increase of moment for the different halides in terms of the size of the halogen atom and an effect of the hydrocarbon chain upon the field of the primary dipole, but no quantitative explanation has been advanced. Their careful calculation[9] of inductive effects, which involves the fundamental uncertainties inherent in earlier calculations, gives a moment increase from methyl to ethyl chloride of 0.11×10^{-18} as compared to 0.18 observed, for the bromides, an increase of 0.11 calculated as compared to 0.21 observed, and, for the iodides, 0.10 as compared to 0.23 observed. Their calculated increase from ethyl chloride to *i*-propyl chloride, which is caused by increase in the amount of polarizable matter within the effective range of the C−Cl dipole, is 0.07 as compared to an observed 0.10, and, for the bromides, the calculated increase is 0.06 as compared to 0.18 observed. The increase in moment from normal to secondary butyl chloride should be approximately the same as that from *n*-propyl to *i*-propyl. The value observed in the present investigation is 0.03 as compared to 0.05 for the change from *n*-propyl to *i*-propyl chloride and for the change from normal to secondary butyl bromide observed by Groves and Sugden. The further increase observed from secondary to tertiary butyl chloride

[8] C. P. Smyth, *Dielectric Constant and Molecular Structure* (The Chemical Catalog Company, New York, 1931), pp. 75, 102.

[9] L. G. Groves and S. Sugden, J. Chem. Soc. 1992 (1937).

is only 0.01, an amount too small to establish the existence of the increase which is to be expected because of the further increase in the amount of polarizable matter within the effective range of the C−Cl dipole. The increase from ethyl to *i*-propyl chloride calculated by Groves and Sugden is approximately $\frac{2}{3}$ of that calculated for the methyl to ethyl increase, while the observed increases, though larger, are in the same ratio as the calculated. The moment induced in each methyl group added to the primary carbon has a considerable component perpendicular to the direction of the axis of the C−Cl dipole. When two methyl groups are present as in *s*-butyl chloride, these two components, making a wide angle with each other, have a resultant about equal to the contribution of the one component in ethyl chloride. In *t*-butyl chloride, these three components perpendicular to the C−Cl direction cancel one another so that the increase from the primary to the secondary compound should be less than that from methyl to ethyl and the increase from the secondary to the tertiary compound should be less than that from the primary to the secondary.

The much larger size of the increase in the apparent moment values observed in solution, in benzene or heptane, 1.97 for *n*-butyl chloride, 2.09 for *s*-butyl chloride, and 2.15 for *t*-butyl chloride was due to solvent effect. It has been shown by Higasi[10] and by Frank[11] that, when the axis of the molecular dipole lies in the longest axis of the molecule, the moment observed for the molecule in solution is lower, because of inductive effects, than that observed in the vapor state, while, if the dipole axis lies perpendicular to the longest axis of the molecule, the apparent moment value observed in solution is higher than that observed for the gas. Because of possible rotation around the C−C bonds in the butyl chlorides, it is difficult to establish with any precision the position of the longest axis of the molecule relative to the principal dipole, that in the C−Cl bond, but it appears fairly certain that the dipole is, on the average, more nearly parallel than perpendicular to the longest molecular axis. Consequently, the apparent moment observed in solution should be lower than the gas value, as found. Change from the primary to the secondary butyl chloride lessens the difference between the molecular dimensions in different directions and, therefore, lessens the difference between the gas value of the moment and the apparent solution value. Finally, the *t*-butyl chloride molecule is so nearly spherical in form that the molecular dimensions are nearly the same in all directions. Consequently, the solution value of the moment should be indistinguishable from the gas value as found.

The solution values[8] for the moments of *i*-butyl chloride, bromide and iodide are identical with those for the corresponding normal compounds. Shortening of the molecule through branching of the chain may have lessened the lowering of the apparent moment by solvent effect, raising the solution values of the *i*-butyl halides to equal those for the *n*-butyl and thus accounting for the failure to observe differences like the small difference between the gas values for *i*-butyl and *n*-butyl chloride in Tables II and III. The branching of the chain in the *i*-butyl group is so far from the C−Cl dipole that one would, at first glance, expect it to have very little effect upon the moment of the molecule, the change, if any, being a slight increase due to the added amount of polarizable material near the limit of the effective inductive action of the C−Cl dipole. The small but appreciable decrease observed in the *i*-butyl chloride moment as compared to that of *n*-butyl chloride is, however, not inconsistent with the appearance of the molecular model, for, of the different positions possible for the two methyl groups through rotation around the carbon-carbon bonds of the molecule, a large fraction places these groups in the neighborhood of the C−Cl dipole where they would make such angles with the axis of the dipole that the moments induced in them would oppose that of the inducing dipole and thus tend to reduce the observed molecular moment. Such an inductive effect probably accounts for the lowering of the moment of *i*-butyl alcohol 0.05×10^{-18} below that of *n*-butyl alcohol.[7]

The moment 1.77 obtained for methyl chloroform in Table II is about 0.8×10^{-18} higher than

[10] K. Higasi, Sci. Pap. Inst. Phys. Chem. Res. (Tokyo) **28**, 284 (1936).
[11] F. C. Frank, Proc. Roy. Soc. (London) **A152**, 171 (1935).

that of the chloroform molecule. It should be higher than the latter because of the inductive action of each of the three C−Cl dipoles upon the methyl group. On the other hand, these three dipoles, because of their mutual inductive action, should be somewhat smaller than the C−Cl dipoles in methyl and ethyl chloride, thus accounting for the much lower moment of chloroform as compared to methyl chloride. The moment induced in the methyl group by each of the three C−Cl dipoles should, therefore, be smaller than the similarly induced moment in the methyl group of ethyl chloride. Moreover, each of these induced moments will have a component perpendicular to the C−C line and, in methyl chloroform, these three components perpendicular to the C−C line will cancel one another. The increase in moment of methyl chloroform over chloroform should, therefore, be considerably less than three times the increase, 0.18×10^{-18}, from methyl to ethyl chloride. These considerations have neglected possible change in the small H−C bond moment, although Raman spectra show a slightly tighter binding of the H−C bond in chloroform than of those in the methyl group in methyl chloride.[12] Electron diffraction shows no abnormality in the C−Cl bonds in chloroform[13] such as has been found in the carbon-halogen bonds in the fluoromethanes and fluorochloromethanes.[14] Increases in moment analogous to that from chloroform to methyl chloroform have been found in the solution values for 1,1-dichloroethane, 1,1-dichloropropane, and 2,2-dichloropropane[15] as compared to that for methylene chloride, the increases again being somewhat larger than those estimated. The roughly quantitative treatment of these increases in moment does not establish induction as the only cause of the increases, but it does indicate it to be a major cause.

The calculations of Groves and Sugden[9] of the inductive effects in nitromethane and nitroethane, in which they use a single resultant moment for the C−N and the two N−O dipoles, are in agreement with the small rise which they observe from the methyl to the ethyl compound. This is in contrast to the markedly higher observed than calculated values in the case of the alkyl halides. In view of the smallness of the rise from the methyl to the ethyl compound in Table III, the absence of rise in the values of Groves and Sugden for the propyl and butyl compounds is to be expected. However, their treatment of the small C−N dipole and the two large N−O dipoles as a single resultant dipole introduces an added element of uncertainty not present in their calculations of inductive effects in the alkyl halides, so that there should be a possibility of error in these calculations even greater than those in the treatment of the alkyl halides, where the calculated increases were considerably smaller than the observed. The much larger increase in moment from nitromethane to α-nitropropane observed in the present investigation is not, therefore, to be regarded as necessarily conflicting with structural considerations, although the reason for the difference between this value and that found by Groves and Sugden is not apparent. Examination of models of these molecules shows that the two methyl groups in β-nitropropane and the three methyl groups in 2-methyl-2-nitropropane must, on the average, spend a good part of the time in positions at such angles to the axis of the nearer of the two N−O dipoles that this will induce moments in them partially opposing the resultant molecular moment. The amount of this opposition of the induced moments could be quite sufficient to cancel the contributions of moments induced in the direction of the principal moment. It is reasonable, therefore, that the molecules of α-nitropropane, β-nitropropane, and 2-methyl-2-nitropropane should have moments indistinguishable from one another, although these considerations are not sufficiently exact to predict their identity.

The authors wish to express their gratitude to the Commercial Solvents Corporation and to Professor R. H. Ewell of Purdue University for some of the substances used in these measurements.

[12] J. H. Hibben, Chem. Rev. **18**, 14 (1936).
[13] L. O. Brockway, Rev. Mod. Phys. **8**, 231 (1936).
[14] L. O. Brockway, J. Phys. Chem. **41**, 747 (1937).
[15] P. M. Gross, Physik. Zeits. **32**, 587 (1931).

The Vapor Density of Iodine at High Temperatures

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By measurement of pressure-volume products of iodine vapor at temperatures between 723°K and 1274°K, it was determined that the vapor in this region consists of diatomic molecules and atoms in equilibrium. No evidence was found for the existence of triatomic molecules. The heat of dissociation of iodine, calculated from the experimentally determined equilibrium constants and the known energy levels of the I atom and the I_2 molecule, was found to be 35,514±50 calories. This is in good agreement with the value obtained by Brown from spectroscopic data alone, $\Delta H_0^0 = 35{,}547 \pm 20$ calories. Other quantities calculated were $\Delta F^0_{298.1°K} = 28{,}882 \pm 50$ calories and $\Delta H^0_{298.1°K} = 36{,}057 \pm 50$ calories.

IT has been known for a long time that iodine vapor at ordinary temperatures consists of diatomic molecules. Dissociation of these molecules, which at 600°C and atmospheric pressure amounts to several tenths of one percent, increases with rising temperature reaching a value of fifty percent in the neighborhood of 1200°C.

Although this equilibrium, represented by the equations

$$I_2 = 2I, \quad K = f_I^2/f_{I_2}, \tag{1}$$

has been investigated by three sets of workers,[1–3] Starck and Bodenstein alone succeeded in obtaining reasonably good results. Even their constants, which cover a range of about two in concentration over the temperature interval between 800°C and 1200°C show what seems to be a trend with pressure. Correction of the constants for gas imperfection would magnify this trend. Moreover, the rough calculations of Rollefson and Eyring[4] indicate that triatomic halogen molecules, whose existence has been proposed in certain reaction mechanisms,[5] may be sufficiently stable for detection by vapor density measurements.

In order to ascertain whether or not the Eqs. (1) represent completely the state of iodine vapor—that is in order to determine whether the constants from (1), calculated assuming the presence of only two molecular species, are true constants at any given temperature, and whether the constants at the various temperatures give the same value for the heat of dissociation in the standard state at 0°K—experimental work of a hoped for higher degree of accuracy than that previously attained was undertaken.

METHOD

The apparatus, shown diagrammatically in Fig. 1, was designed to make direct measurements of pressure-volume products. The resistance type Alundum tube furnace *A* (Fig. 2), which maintained the clear fused silica bulb *B* at any desired temperature, was wound with 45

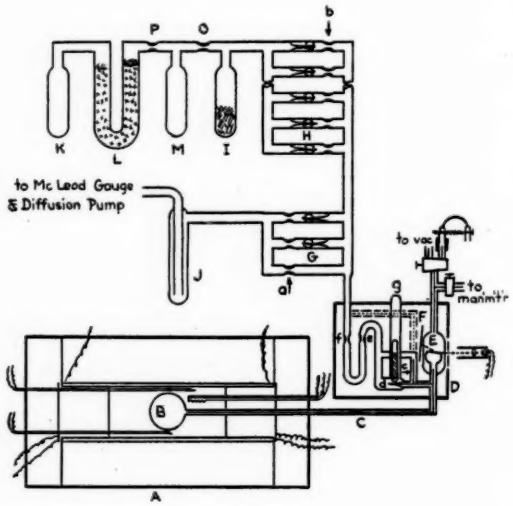

FIG. 1.

[1] Starck and Bodenstein, Zeits. f. Elektrochemie **16**, 961 (1910).
[2] Braune and Ramstetter, Zeits. f. physik. Chemie **102**, 480 (1922).
[3] DeVries and Rodebush, J. Am. Chem. Soc. **49**, 656 (1927).
[4] Rollefson and Eyring, J. Am. Chem. Soc. **54**, 170 (1932).
[5] G. K. Rollefson, *The Photochemistry of the Halogens* (Hermann and Company, Paris), 1938.

turns (4 ohms) of No. 8 Chromel wire embedded in refractory cement. At the ends of the 24-inch tube independently controlled heaters of Kanthal wire were installed to eliminate, as far as possible, temperature gradients in the working space. For the same reason there was placed inside the Alundum tube a liner, over one-half inch in wall thickness, cast of Calite *A*, an iron-nickel-chromium oxidation-resistant alloy, which was fabricated by the Calorizing Company, Pittsburgh, Pennsylvania. Two heavy Calite disks, separated by Sil-O-Cel insulating material, closed each end of the liner. Surrounding the whole was approximately 4 inches of granular Sil-O-Cel. The silica bulb was covered with platinum foil to prevent falling oxide particles from fusing into it at high temperatures.

The 2-mm silica capillary leading from the bulb was connected through a graded seal *C* to Pyrex capillary, which led to the all-glass system shown in the diagram. The capillary tubing was wound with resistance wire and asbestos tape so that it could easily be maintained at about 300°C. An oven *D*, electrically heated to 200°C and thermostated to $\pm\frac{1}{2}$°C with a De Khotinsky regulator, contained a Pyrex click gauge *E*[6] for measuring the gas pressure inside the furnace; a U-tube in which the iodine could be condensed; and a break-off, whose glass-enclosed hammer was operated by means of a magnet. In the side of the oven was a double Pyrex window through which a light beam reflected from the surface of the click gauge onto the screen *F* could be observed. The position of the spot of light indicated whether the gauge was "in" or "out."

C represents two break-offs by means of which the system was opened to or sealed off from the pumps. A set of ten break-offs in parallel *H* served to admit iodine into the system from the reservoir *I* where it was stored. The trap *J* was always kept cooled in liquid air. The purification train *KLM* was detached at 0 after it had served its purpose.

The temperatures of the iodine vapor were measured with a platinum (90 percent platinum–10 percent rhodium), thermocouple which was calibrated by the National Bureau of Standards to accuracy of ±2°C. A check of this thermocouple at the melting point of silver, and the fact that the calibration of the Bureau did not at any point in the range used deviate more than 1° from the data given in the *International Critical Tables* make it seem quite likely that the temperatures as read were accurate to 1°. A long platinum (87 percent platinum–13 percent rhodium) thermocouple was used to measure gradients in the working space. In order to be certain that no immersion effects were being mistaken for gradients, the thermoelement was inserted from both ends of the furnace, so that it was possible to determine the temperature of any point with two depths of immersion. Radial temperature differences were less than 0.7°C. The difference in temperature between the center and the cooler end of the bulb was never over 2°; since the bulb was spherical it is estimated that 80 percent of the bulb volume was within 1° of the temperature at the center. The temperature taken for that of the gas was found by weighting the gradients over the bulb. Through the course of the experiments the difference between the electromotive forces of the two thermocouples

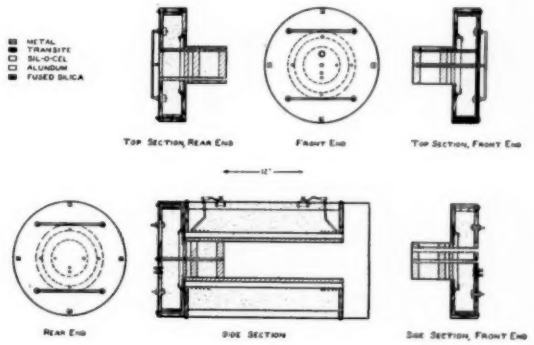

FIG. 2. Furnace.

at any temperature remained constant to within one or two microvolts (0.1°–0.2°C). The thermocouple readings always checked, in addition, with the resistance thermometer, which was part of the furnace temperature regulator.

Electromotive forces were measured with a Leeds and Northrup Type K-2 potentiometer. This instrument, the galvanometer, and the cells were supported on glass plates which were placed on grounded metal sheets. To prevent leakage

[6] Smith and Taylor, J. Am. Chem. Soc. **41**, 1393 (1924).

TABLE I. *Temperature coefficient of click gauge constant.* Gauge No. 10.*

TEMPERATURE (°C)	C. G. CONSTANT (CM Hg)	TEMPERATURE (°C)	C. G. CONSTANT (CM Hg)
22	2.75_0	110	2.78_5
46	2.76_5	140	2.80_0
74	2.76_5	180	2.81_5

* The cathetometer used in this set of measurements had a precision of only 0.01 cm Hg.

between the heater circuits of the furnace and the thermocouple it was found necessary to ground the inside metal parts.

A platinum resistance thermometer in conjunction with the thyratron-controlled regulator described by Benedict[7] was used to thermostat the furnace. During a series of measurements lasting from one to two hours the temperature remained constant to 0.1° or 0.2°C.

The temperatures of the capillary outside the furnace were measured by three Chromel-Alumel thermoelements wrapped directly on the glass. Experiments showed that temperatures so obtained are the same within a degree or two as those inside the capillary. The temperatures of the quartz capillary leading through the end of the furnace were determined by exploration with the long noble-metal thermocouple.

The volume of the bulb, as found by weighing with water and making all necessary corrections, was 342.64 cc before the start of measurements and 342.71 cc afterwards. The average was used in the calculations. Data for correction of the volume for thermal expansion were taken from the "I.C.T." The obnoxious volume, measured by weighing with mercury, was such as to contain from 3 percent to 5 percent of the total iodine sample. Error in the obnoxious volume correction, it is estimated, causes an uncertainty of about 0.05 percent in the amount of iodine calculated to have been in the furnace bulb.

In order to measure accurately the external air pressure required to just click the diaphragm gauge "in" it was necessary to have the applied pressure increase slowly. An auxiliary manometer and a variable leak, which has been described,[8] were used to set the rate of increase at about 0.1 mm of mercury every 2 or 3 seconds. Changing this rate did not affect the measured pressure. A stopcock was inserted into the line to cut off the main manometer at the proper instant. The difference in height between the mercury menisci of this manometer[9] was compared with a standard meter bar by use of a Gaertner cathetometer having a precision of better than 0.005 cm. Meniscus corrections were taken from the work of Cawood and Patterson.[10] The densities of mercury were taken from the *International Critical Tables*.[11] The standard acceleration of gravity was taken as 980.665 cm/sec.^{2}, and the acceleration of gravity for this location was taken as 979.973 cm/sec.^{2}.[12]

TABLE II. *Successive determinations of C. G. constant at 200°C. Gauge No. 2.*

TRIAL	C. G. CONSTANT (CM Hg)	TRIAL	C. G. CONSTANT (CM Hg)
1	2.51_3	3	2.50_7
2	2.50_9	4	2.50_8

Experiments were undertaken to make certain that pressure measurements accurate to 0.01 cm of Hg or better could be obtained with click gauges under the conditions to which it was necessary that they be exposed. It was found that the pressure difference required to click a gauge is constant and independent of the pressure inside the gauge to less than 0.01 cm of Hg at temperatures as high as 200°C. Since a small temperature coefficient of this constant, apparently connected with the elasticity of the glass, was evidenced, the click gauge used was calibrated at its working temperature. Results of some measurements are given in Tables I–III. It should be remarked that the results shown in Table III, the constants for the click gauge used in the main research, were obtained over a period of seven weeks. During this time the gauge was maintained at 200°C for over 225 hours, and it was heated to this temperature from room temperature about twenty-five times.

All substances used in the preparation and purification of iodine were of reagent quality

[7] Benedict, Rev. Sci. Inst. **8**, 252 (1937).
[8] R. D. Fowler, Rev. Sci. Inst. **6**, 26 (1935).
[9] Giauque and Egan, J. Chem. Phys. **5**, 45 (1937).
[10] Cawood and Patterson, Trans. Faraday Soc. **29**, 1522 (1933).
[11] Int. Crit. Tab.—Vol. II, pp. 457–458.
[12] Giauque and Kemp, J. Chem. Phys. **6**, 40 (1938).

with the exception of anhydrous $Mg(ClO_4)_2$, which was C.P. The iodine was precipitated by adding dilute H_2SO_4 to a solution containing KIO_3 and KI, the latter in excess. After being washed, the precipitate was dissolved in KI in such a manner that the solution was nearly saturated with both iodine and KI. Dilution of this solution reprecipitated a fraction of the iodine, which was washed eleven times by decantation and allowed to remain over anhydrous $Mg(ClO_4)_2$ for over four months in a desiccator whose lid was lubricated with phosphoric acid. The remainder of the purification process was directed at the elimination of air and of the last traces of water. The iodine was placed in the bulb *K* (Fig. 1) and sublimed three times in vacuum through the anhydrous $Mg(ClO_4)_2$ tube *L*. Light bulbs were used for warming when necessary. Between sublimations the iodine was cooled to about −35°C and pumped on through open break-offs at *H* and *G*. Then, with the iodine in bulb *I*, *K* and *L* were sealed off at the constriction *P*; and two more sublimations were carried out between bulbs *M* and *I*. The small amounts of gas liberated were pumped off as before. Finally, the constriction at *O* and the open break-off at *H* were sealed off. It should be mentioned that before constrictions were melted down, they were always heated to the softening point of the glass and the gases

TABLE III. *Constant of C. G. used in the vapor density measurements. Gauge No. 2 (200°C).*

TIME OF MEASUREMENT		C. G. CONSTANT (CM Hg)
Before run No. 1	6/7/40	2.53_0
Before run No. 2		2.53
Before run No. 3		2.50_3
Before run No. 4		2.49_5
Before run No. 5		2.50_9
After run No. 5	8/1/40	2.49_7

evolved pumped out. The number of break-offs at *H* was sufficiently large so that the iodine was never opened except to high vacuum during the whole course of the experiments.

Before beginning the introduction of an iodine sample into the furnace, points designated *a*, *b*, *c*, *e*, *f* and *g* in the diagram were heated strongly to degas the glass; and the various parts of the system were baked out at their highest working temperatures for a minimum of 36 hours. One of the units of the break-off set *H* was then opened, the iodine reservoir having been previously cooled to −40°C with a freezing mixture. After a few minutes pumping, which sufficed to remove the negligibly small amount of gas accumulated, the open member of set *G* was closed; and iodine was sublimed into the U-tube by cooling it with freezing mixture or liquid air and warming the reservoir with light bulbs. When it was estimated that the sample was of

TABLE IV. *Values of* λ *for* I_2.

TEMPERATURE (°K)	λ	TEMPERATURE (°K)	λ
723	−0.00470	1073	−0.00118
872	−0.00251	1173	−0.00084
973	−0.00170	1274	−0.00060

the desired size, the reservoir was cooled; a member of set *G* was opened; the open member of set *H* was closed; and the constriction *f* was melted down. The iodine was then sublimed into the capillary by surrounding a short length with a small asbestos mat which was kept saturated with liquid air. To hasten this process the oven was warmed. Melting down the capillary by-pass at *c* and replacing the constriction at *f* completed this series of operations. The sample was in only one case correctly estimated; but the first four samples, it turned out, were, though not in order, very nearly of sizes desired. As it was too much to expect this good fortune to continue, for the last run a large quantity of iodine was introduced, and the excess allowed to escape to high vacuum through a capillary leak especially put in for that purpose. This leak is indicated by the dotted lines in the oven *D*.

The pressure of the sample was measured at various furnace temperatures from 1274°K, the first, down to 723°K. Several pressure determinations were made at each temperature. The agreement of successive readings was generally as good as that shown in Table II. To avoid straining or breaking the click gauge while the furnace temperature was being changed overnight, the iodine was allowed to condense in the connecting capillary. In the first run, the equilibrium at 1073°K was approached from different directions at times one week apart; the pressures

were exactly the same after correction by the perfect gas law for the 0.2° temperature difference.

Upon completion of the pressure measurements the constrictions at *a* and *f* were again heated, the open member of set *G* was closed, the U-tube was cooled with liquid air, and the break-off in the oven was opened. The iodine was, of course, at room temperature in the capillary. When raising the liquid-air level showed that no further condensation was occurring (extremely small amounts can easily be detected), the last member of *G* was opened to the McLeod gauge. The noncondensable gas pressure in the furnace vessel was in no case over approximately 5×10^{-3} mm. This and the experiment at 1073°K in the first run demonstrate that diffusion, leakage and degassing were negligibly small. The stopcock to the pumps was then opened and the capillary warmed. The level of the liquid air on the U-tube was raised at every operation, but no more iodine was ever observed to come over. Finally, the tube was melted off at *f* and *e*. For the next run new units were installed at *G* and in the oven *D*; and the small part (about 0.2 cc) of the obnoxious volume in the old unit was measured by filling it with water from a small burette.

It was necessary, then, to determine the weight of iodine in the sample. The bend of the U-tube was scratched on the outside with a file. The tube and a tall, light weighing bottle into which it fitted were thoroughly cleaned and, after being placed under high vacuum overnight, weighed. The tube was then cracked open inside the bottle by use of a screw clamp. Care was taken to prevent particles of glass from flying out upwards. When the bottle and broken tube had been pumped out overnight to remove the iodine, they were reweighed. The necessary buoyancy corrections were made.

TABLE V. *Analyses of iodine samples.*

Sample No.	*P*(Atmos.)	Moles in Obn. Vol. $\times10^5$ (as I_2)	Tot. Moles by Gas* $\times10^3$ (as I_2)	Moles by Wt. $\times10^3$ (as I_2)
4	0.04343	0.572	0.2568	0.2554
2	0.21542	2.85	1.2749	1.2725
3	0.35626	4.72	2.1099	2.1055
5	0.44703	5.94	2.6488	2.6447
1	0.59212	7.73	3.5095	3.5083

* Uncorrected for dissociation.

An experiment in which all operations except opening the break-off to the iodine reservoir were performed showed a loss in weight of only 0.0001 gram.

Each complete run, after the technique had been mastered, required about one week.

Results

The atomic weight of iodine was taken as 126.915.[13] The values of all other constants, unless otherwise stated, were those of the "I.C.T." Although the results were affected but little, correction was made for gas imperfection of I_2. Monatomic iodine was assumed to be a perfect gas. Some justification is perhaps offered for this assumption by the results of the application of Berthelot's equation of state to xenon.

The critical pressure of iodine is not recorded. An estimated value of 116 atmospheres was obtained by use of the principle of corresponding states with the known critical temperature and boiling point of iodine, 826°K and 457°K, respectively, and the vapor pressure and critical data for chlorine. This estimate was used in Berthelot's equation and the constant λ of that equation in the form

$$PV=RT(1+\lambda P) \qquad (2)$$

was calculated at the various furnace temperatures.

The regulator which thermostated the furnace permitted fairly easy reproduction of temperatures to within less than 0.5°. A small correction, based on the perfect gas law, was applied to the measured pressures so that they corresponded to a set of mean temperatures chosen for all the runs (Table IV).

The obnoxious volume was divided into five regions at different temperatures to enable calculation of the amount of iodine in it to be made more accurately. Corrections were made for dissociation in that part of the capillary leading through the end of the furnace; the perfect gas law was applied to the remainder. The total quantity thus obtained was divided by $(1-0.013P)$, an average factor for the whole

[13] Baxter and Titus, J. Am. Chem. Soc. **62**, 1826 (1940).

TABLE VI. *Constants for the reaction* $I_2 = 2I$.

RUN NO.	T(°K)	P(ATMOS.)	$M \times 10^5$	P_{theor} (ATMOS.)	α'	K	ΔH_0^0(CAL.)
4	1274	0.11216	1.365	0.07363	0.5233	0.1692	35,494
2	1274	0.47416	5.93	0.36950	0.28325	0.1657	35,547
3	1274	0.75308	9.35	0.61284	0.22884	0.1671	35,526
5	1274	0.93082	11.49	0.77055	0.20799	0.1692	35,494
					Mean±av. dev.		35,515±21
4	1173	0.09181	1.14	0.06844	0.3415	4.847×10^{-2}	35,483
2	1173	0.40087	5.05	0.34273	0.16964	4.769	35,521
3	1173	0.64446	8.06	0.56797	0.13467	4.798	35.507
5	1173	0.80042	9.99	0.71380	0.12135	4.836	35,488
1	1173	1.04680	13.19	0.94705	0.10533	4.773	35,519
					Mean±av. dev.		35,504±14
4	1073	0.07500	0.96	0.06309	0.1888	1.110×10^{-2}	35,489
2	1073	0.34287	4.37	0.31531	0.08741	1.065	35,577
3	1073	0.55807	7.08	0.52214	0.06881	1.082	35,543
5	1073	0.69640	8.97	0.65566	0.06214	1.108	35,492
1	1073	0.91672	11.66	0.87037	0.05325	1.084	35,539
					Mean±av. dev.		35,528±30
4	973	0.06244	0.80	0.05757	0.08459	1.805×10^{-3}	35,578
2	973	0.29815	3.84	0.28719	0.03816	1.785	35,600
3	973	0.48982	6.20	0.47558	0.02994	1.855	35,525
5	973	0.61283	7.93	0.59704	0.02645	1.852	35,529
1	973	0.80970	10.27	0.79258	0.02160	1.709	35,684
					Mean±av. dev.		35,583±47
4	872	0.05346	0.69	0.05184	0.0313	2.11×10^{-4}	35,486
2	872	0.26138	3.40	0.25833	0.01181	1.62	35,944
3	872	0.43143	5.61	0.42751	0.00917	1.81	35,752
5	872	0.54123	7.05	0.53698	0.00791	1.86	35,704
1	872	0.71671	9.24	0.71256	0.00582	1.66	35,901
					Mean±av. dev.		35,757±132

dead space derived from Eq. (2), to give the quantity used in the calculations.

Pressure measurements were made at a furnace temperature of 723°K to check the weight analyses of the iodine samples. Equation (2) was used to calculate the number of moles in the bulb. The results, given in Table V, show excellent agreement between the methods of analysis, especially when the very small dissociation constant,[14] $K_{723°K} = 2 \times 10^{-6}$ is taken into account.

Equilibrium constants (Eq. (1)) at the other furnace temperatures—1274°K, 1173°K, 1073°K, 973°K, 872°K—were calculated in terms of fugacities. If the following assumptions[15] are made: (a) $P_{I_2}V = nRT(1+\lambda P)$, where P is the total pressure of the gaseous mixture of I_2 and I, (b) monatomic iodine is a perfect gas, (c) the partial pressure of any component of a gaseous mixture is the product of its mole fraction and the total pressure, (d) the fugacity of any component of a gaseous mixture is the product of its mole fraction and the fugacity that that component would have if it were at the total pressure of the mixture, then the expression for the equilibrium constant is found to be

$$K = \frac{4P(\alpha' - \lambda P)^2}{(1-\lambda P) - (\alpha' - \lambda P)^2(1+\lambda P)},$$

where α' is the degree of dissociation neglecting gas imperfection. The quantity α' was evaluated from the expression $\alpha' = \Delta P / P_{theor}$, in which P_{theor} is the pressure that the amount of iodine in the bulb would have if it were a diatomic, perfect gas, and ΔP is the difference between

[14] Murphy, J. Chem. Phys. **4**, 344 (1936).
[15] Lewis and Randall, *Thermodynamics and the Free Energy of Chemical Substances* (McGraw-Hill Book Company, New York, 1923), p. 225.

this pressure and the actual pressure. The amount of iodine in the bulb was found by subtracting the amount in the obnoxious volume from the number of moles by weight in the total sample. The results are given in Table VI. The symbol M is used to represent the number of moles of iodine, expressed as I_2, in the obnoxious volume.

By substituting into the equation

$$\Delta F^0/T = -R \ln K = \Delta(F^0 - H_0^0/T) + \Delta H_0^0/T, \quad (3)$$

TABLE VII. *Final value of* ΔH_0^0 *for* $I_2 = 2I$.

TEMPERATURE °K	ΔH_0^0(CAL.)	WEIGHT
1274	35,515±25	160
1173	35,504±30	111
1073	35,528±55	33
973	35,583±140	5
872	35,757±480	0.4
Weighted result $\Delta H_0^0 = 35{,}514 \pm 18$ cal.		

the experimentally determined equilibrium constants and the known $(F^0 - H_0^0)/T$ functions—derived from spectroscopic data—for the I atom and the I_2 molecule, the value of ΔH_0^0, the heat in the standard state at 0°K, for the reaction $I_2 = 2I$ may be calculated. The values of $(F^0 - H_0^0)/T$ for atomic iodine were obtained for the necessary temperatures from the equation

$$-(F^0 - H_0^0)/T = (3/2)R \ln M + (5/2)R \ln T + R \ln Q - 7.267.$$

Murphy has evaluated the corresponding function for the iodine molecule from spectroscopic data and expressed the results in an empirical equation of the form

$$-(F^0 - H_0^0)/T = a/T + b \log T + cT + dT^2 + i.$$

The values of ΔH_0^0 given refer to the lowest observable state of the I_2 molecule.

The mean values of ΔH_0^0 given in Table VI have appended to them the average deviations. In Table VII there is appended, instead, what is more likely to be the error—namely, the change that would be brought about in the value of ΔH_0^0 by an error of 1° in the temperature measurement on the average sample. Such an error is not unlikely in view of the possible error of one degree in the calibration of the thermocouple and the uncertainty in the temperature scale in the region of the measurements. To find the final value of ΔH_0^0 the mean values were given weights based on these errors.

The application of statistical methods to the calculation of the error for such a limited number of observations might be questioned, therefore a brief consideration of possible errors is desirable. If no correction is made for the deviations of the iodine molecules from the perfect gas laws, but the data are otherwise treated the same, the weighted average for ΔH_0^0 is found to be 35,539±18 calories. Hence no great error can be introduced by errors in the corrections for gas imperfections. The use of spectroscopic data in the calculation of $(\Delta F^0 - \Delta H_0^0)/T$ involves the values of certain physical constants. The final result for ΔH_0^0 is not very dependent on these values; if the latest values given by Birge (Table IX) are used instead of those in the *International Critical Tables* the value of ΔH_0^0 is changed by only two calories. The spectroscopic determinations of the vibrational and rotational levels are so accurate that no appreciable error can be introduced in that way. It is concluded, therefore, that the error indicated is reasonable but to be conservative an arbitrary choice is made of a value of fifty instead of eighteen calories as the uncertainty in ΔH_0^0.

With this value of ΔH_0^0 in Eq. (3), $\Delta F^0_{298.1°K}$ was found to be 28,882±50 calories. By differ-

TABLE VIII. ΔH_0^0 *for the reaction* $I_2 = 2I$ *from previous investigators.*

INVESTIGATOR	TEMPERATURE °K	ΔH_0^0 (CAL.) MAXIMUM	MINIMUM	MEAN±AV. DEV.
Starck and Bodenstein[1]	1472	35,593	35,355	35,479± 90
	1373	35,616	35,368	35,461± 78
	1273	35,687	35,309	35,530± 92
	1173	35,879	35,337	35,542±136
	1073	36,058	35,040	35,456±234
De Vries and Rodebush[3]	898	36,015		
	873	35,849		
	848	35,858		
	823	35,639		
	794	35,665		
	732	35,015		
Braune and Ramstetter[2]	1384	34,542		
	1344	37,595		
	1260	36,935		
	1097	36,012		
	1021	35,933		
	999	35,571		
	915	35,395		

TABLE IX. *Values of physical constants. Birge (August, 1939).*

Electronic charge	$e=(4.8022\pm0.0010)\times10^{-10}$ abs. e.s.u.
Faraday constant (chemical scale)	$F=(2.89224\pm0.00031)\times10^{14}$ abs. e.s.u.·g-equiv.$^{-1}$
Velocity of light	$c=(2.99776\pm0.00004)\times10^{10}$ cm·sec.$^{-1}$
Planck constant (obtained by substitution of e and e/m in Rydberg constant formula).	$h=(6.62365\pm0.0024)\times10^{-27}$ erg·sec.
Avogadro number	$N=F_c/e=(6.02274\pm0.0014)\times10^{23}$ mole^{-1}

entiation of Eq. (3) $\Delta H^0_{298.1°K}$ was calculated as 36,057±50 calories. These two values give $\Delta S_{298.1°K}$ the value 24.08 entropy units.

For comparison values of ΔH_0^0 were calculated from the equilibrium constants of other investigators,[1–3] see Table VIII.

The value of ΔH_0^0 may be calculated directly by extrapolation of spectroscopic data. This has been done by three investigators.[16–18] The work of Brown, who alone used the Birge-Sponer extrapolation to the convergence limit, appears to be the most reliable.[19] This value, 12,439±3 cm^{-1}, converted to calories per mole with the aid of the "I.C.T." constants, is 35,405±23 calories. Some of these constants, it has been definitely established, are in error. If the latest values given by Birge[20] (Table IX) are used instead, it is found that $\Delta H_0^0=35{,}547\pm20$ calories, which is in good agreement with the value resulting from this research.

[16] G. E. Gibson and W. Heitler, Zeits. f. Physik **49**, 465 (1928).
[17] Kuhn, Zeits. f. Physik **39**, 77 (1926).
[18] Brown, Phys. Rev. **38**, 709 (1931).
[19] G. E. Gibson, private communication.
[20] Birge, "Values of general physical constants," mimeographed sheets, University of California (August, 1939).

The result of Brown, 12,439 cm^{-1}, may be equated to the value obtained in this research according to the equation

$$12{,}439hcF_c/e=148{,}624\times10^7.$$

By insertion of the values given above for F_c, c, and J_{15}, a value for h/e may be obtained. It is found that $h/e=(1.378\pm0.002)\times10^{-17}$ erg·sec.·e.s.u.$^{-1}$. The value given by Birge, which is derived from the Rydberg constant, is $h/e=(1.37929\pm0.00023)\times10^{-17}$ erg·sec.·e.s.u.$^{-1}$.

The absence of trends in the values obtained for ΔH_0^0 indicates that the equation

$$I_2=2I$$

represents the condition of iodine vapor in the temperature region covered by these experiments. Rough calculations fix the upper limit of the concentration of triatomic iodine molecules in this region at about 0.3 mole percent.

We wish to express our gratitude to Professors R. T. Birge and W. F. Giauque for much helpful discussion of the calculations.

Thermal Diffusion in Ternary Liquid Mixtures, Particularly Aqueous Solutions Containing Ferrous Chloride*

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The accumulative arrangement of Clusius and Dickel for thermal diffusion was used to study the concentration changes at the extreme ends of the apparatus that occur in various mixtures, particularly solutions of two solutes in water. The apparatus gave reasonably reproducible results. To avoid uncertainties due to creeping along the upper part of the hot wall, any apparatus intended for the study of slightly soluble substances should be designed, as was the apparatus used, so that it can be filled without leaving an air space between hot and cold wall. The enrichment of acetic acid in water solution at the cold (and lower) end is rather small, compared with that of glycerine, or many salts or strong acids. Addition of sodium acetate does not greatly affect the enrichment of acetic acid. The enrichment of ferrous chloride in water at the cold end is considerable, but in the presence of $1M$ HCl the enrichment occurs at the hot end. In the presence of $1N$ H_2SO_4 the enrichment was zero. The case is opposite with zinc chloride. Here the small cold-end enrichment that occurs in the presence of a trace of acid to prevent hydrolysis is considerably increased in the presence of $1M$ HCl. In a solution of ferric chloride and $1M$ HCl the enrichment of iron was also at the hot end. Hydrolysis takes place, but this probably works against such a result. It appears that a heavy constituent of a ternary liquid solution can migrate from cold to hot end, against the direction normally expected. A simple function of the composition is given whose sign is the same as the sign of the enrichment at the cold end in all binary mixtures (liquid or gaseous) so far studied, but not always the same in ternary mixtures.

INTRODUCTION

THE arrangement of Clusius and Dickel[1] for producing separation by thermal diffusion works by combination of thermal diffusion along a horizontal thermal gradient between two vertical walls and convection along these walls. The arrangement used by various investigators of the Soret effect utilizes a vertical thermal gradient, the higher temperature being maintained above in order to avoid convection.

The arrangement of Clusius and Dickel may be regarded as a means for multiplying the Soret effect and offers a sensitive means of studying it. Unfortunately the factor by which the Soret effect is multiplied is not readily determinable, so that interpretation in terms of Soret effect can be only semiquantitative. Nevertheless, we have tried to investigate the behavior of some ternary mixtures containing water and two solutes, with respect primarily to the question whether the behavior of each of the solutes is independent.

APPARATUS

The arrangement was used in the form of two concentric glass tubes, steam being passed through the inner, and cooling water through the outer, the solution under investigation being in the annular space between the two tubes. Brewer and Bramley[2] have used this form. The Pyrex diffusion apparatus is shown in Fig. 1. The tubes for enclosing the annular space were selected as the best pair from about 100 samples and built into apparatus No. 1. The width of the annular space (along a radius) is about 0.75 mm, the total length about 1 meter and the capacity of annular space plus dead space at top and bottom about 71 cc. The next best pair of tubes was built into apparatus No. 2. The width of annular space is about 1.25 mm, the length 1 meter and the capacity about 85 cc. Apparatus No. 2 gave considerably smaller separations in every solution used for comparison and only a few experiments are here reported with it.

In July the cooling water entered (the bottom) at 20° and left at 32°, constant to about 0.5° for days. This would make the mean temperature difference of the outside surfaces of the walls 100−26 or 74°. In winter this difference increased to 80° and rarely 85°.

Some preliminary experiments with 10 percent (by weight) of glycerine showed with neither

* Contribution No. 463 from the Research Laboratory of Physical Chemistry. This is principally based on the thesis presented by Mr. Breck for the B.S. degree.

[1] K. Clusius and G. Dickel, Naturwiss. **26**, 546 (1938).

[2] A. K. Brewer and A. Bramley, Phys. Rev. **55**, 590 (1939).

apparatus any difference with time from 22 to 43 hours. In later experiments a comparison of results for different lengths of time was often possible and there was no indication that more than 24 hours was required for the steady state, unless possibly in some solutions containing three solutes.

Filling the Apparatus

For all the experiments but the last three the annular space was filled so that the solution stood during the experiment at about the level of the cooling water. This left a small air space above the liquid. The upper filling tube was closed with a glass cap and wax after the steady temperature was reached. This prevented evaporation or oxidation.

The air space allowed salts to creep up along the hot wall. There the liquid film evaporated, the solvent passing to the cold wall. With solutions containing $BaCl_2$ creeping was very considerable and the results are not stressed. In the case of the other salts (except $ZnCl_2$) creeping occurred, but to a very small extent—the deposit was estimated to amount to not more than 0.1 gram. The rate at which the fluid is circulated along the walls is very considerable and it would seem that the small loss of material should occur at the expense of both hot and cold ends of the tube, without particular prejudice to either.

Nevertheless, the results for ferrous chloride in mixtures were so unexpected that three experiments (here reported as the last three items of Table I) were done after the completion of all the other work, when we found that the apparatus can be filled so that no air space is in contact with the hot wall and creeping is therefore prevented. Since the volume of the upper dead space is considerably greater by this manner of filling, a longer time was allowed for diffusion to take place.

Sampling

After the diffusion, a sample of about 1 cc was taken from the top with a small capillary pipette. When cool, a portion of about 0.3 cc was accurately measured in a special pipette. A sample of about 1 cc was taken from the bottom after wasting 6 drops to clear the stopcock leads. In each of the last three experiments of Table I about 1.5 cc was taken and 1 cc used for analysis. Samples from the middle were sometimes taken with a long capillary pipette and sometimes through the stopcock after discarding a large portion. When the transfer of component is small, the middle portion agrees in composition with the original solution used for filling and was often taken as a measure of it.

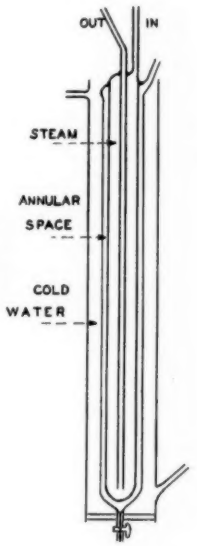

Fig. 1. Diffusion apparatus. A cork stopper was actually used instead of the higher of the two ring seals, but it requires frequent replacement, because of the action of the steam.

In the case of solutions containing HCl and $FeCl_2$ that diffused for 4 days, samples from levels one-third down the tube and two-thirds down showed large changes of acidity from the original, and the original titer was used as a basis. The titers for ferrous iron from these levels gave a welcome check on the titer of the original mixture.

Analysis

Measurements of refractive index were used for solutions of glycerine and of acetic acid, as noted below.

In solutions containing iron, ferrous iron was determined by permanganate titration. Since chloride was present the method was checked by analysis of known mixtures. Ferric iron was determined from the titer for ferrous iron and the titer for total iron as found after reduction with SO_2 and removal of excess SO_2. In mixtures of $FeCl_2$ and HCl the acid was first determined

by titration with sodium carbonate in the presence of bromphenolblue (without any precipitation of iron) and the ferrous iron then determined by permanganate in the same sample, a stream of nitrogen being used throughout to prevent oxidation. In mixtures containing ferric iron the acidity was not determined.

In the analysis of mixtures of $ZnCl_2$ (or $BaCl_2$) and HCl the hydrogen ion was first titrated in the presence of methyl red. The total chloride was then determined by titration with $0.1N$ $AgNO_3$ in the presence of fluorescein as adsorption indicator, and the Zn (or Ba) obtained by difference. When the method was checked by analysis of solutions of HCl a small difference of titer was found (H and Cl). The difference was applied as a correction factor to the results for mixtures of $ZnCl_2$ (or $BaCl_2$) and HCl in order to get the best possible relative accuracy for total chloride.

TABLE I. *Diffusion of solutions containing* HCl, $FeCl_2$ *or* $FeCl_3$ *or combinations in apparatus No. 1.*

Approx. composition of solution	Hours	Component	Per-cent Effect	Titer ratio, cold/hot end
$1M$ HCl	41	H^+	160	9.4
$0.5M$ $FeCl_2$	23	Fe^{++}	22	1.29
Same	31	Fe^{++}	21	1.30
Same	24	Fe^{++}	25	1.32
$1M$ HCl, $0.5M$ $FeCl_2$	29	Fe^{++}	−10	0.90
Same	23	Fe^{++}	−5	0.95
		H^+	190	39.
$0.5M$ H_2SO_4, $0.5M$ $FeCl_2$	25	Fe^{++}	0	1.
		H^+	122	5.0
$1M$ HCl, $0.5M$ $BaCl_2$	24	Ba^{++}	44	1.64
		H^+	106	3.9
$1M$ HCl, $0.5M$ $ZnCl_2$	29	Zn^{++}	30	1.37
		H^+	100	3.7
$0.01M$ HCl, $0.5M$ $ZnCl_2$	29	Zn^{++}	4	1.04
$1M$ HCl, $0.45M$ $FeCl_2$	4×24	Fe^{++}	−13	0.88
		H^+	>180	>19.
Same	4×24	Fe^{++}	−11	0.89
		H^+	194	20.
$0.5M$ $FeCl_2$	4×24	Fe^{++}	22	1.27

Expression of Results

It will be noted that we do not attempt to determine the total transfer of component past some horizontal plane, but only the extremes of concentration at the two ends of the apparatus. The "percent effect" we define to be the titer of the sample from the lower end minus the titer from the upper end, the difference being then multiplied by 100 and divided by the titer of the original sample subjected to diffusion. When the result is negative, this means that the substance is (abnormally) enriched at the upper end.

No "correction" was applied for changes in the average temperature (74–85°, according to the season of the year). The results which we compare were done under nearly the same conditions.

The concentration ratio—lower titer divided by upper—is also of some interest and is reported in Tables I and II. It is not possible to calculate it accurately from the percent effect alone because the mean of the compositions, upper and lower, is often not equal to the original or middle composition.

Results

In apparatus No. 2 a 10-percent (by weight) solution of glycerine in water was subjected to diffusion and the solutions analyzed by the refractive index. The percent effect was 6.44. Samples at 22 and 48 hours showed no difference. Repetition of the experiment gave in 22 hours the percent effect 6.54.

In apparatus No. 1 the same solution showed an effect of 28.8 percent, with no differences in the results at 20, 28 and at 41 hours. A repetition of the experiment gave 35 percent in 22.5 hours.

In apparatus No. 2 a 50-percent solution of glycerine in water showed an effect of 3 percent in 18 hours.

A solution of 62 percent (by weight) acetic acid in water showed no effect by refractive index in either apparatus in 45 hours.

A more dilute solution of acetic acid—10 percent and about 1.7 molal—showed in apparatus No. 1 an effect of 8.1 percent in 22.5 hours, and on repetition an effect of 10 percent in 20.3 hours.

Various mixtures of acetic acid and sodium acetate were prepared and subjected to diffusion in apparatus No. 1. The effect for sodium acetate was determined by the refractive index. A small correction for the refraction of the acetic acid was applied which ignored possible small changes in its concentration. Table II shows the composition of the original solution and the percent effect for sodium acetate. The

transfer of acetic acid was shown to be small or zero by measuring the *p*H of the various samples by means of a glass electrode and by then comparing the observed *p*H with that calculated from the measured concentration of acetate in the sample together with the concentration of acetic acid it would have, were there no transfer of acetic acid. The approximate agreement between observed and calculated *p*H was satisfactory and showed that the transfer of acetic acid is small in the solutions containing sodium acetate.

These results are not sufficient to establish that the acid and the salt in this case diffuse independently but it is very probable that they do so at least approximately.

More interesting results were seen when solutions containing iron chloride were subjected to diffusion. Ferric chloride in water is hydrolyzed at once along the hot wall. This is due to the extensive migration of HCl (formed by hydrolysis) from hot to cold. Ferrous chloride is not hydrolyzed in our apparatus if oxidation is entirely prevented. This is accomplished by leaving a trace of SO_2 in the solution until the apparatus is filled in a stream of nitrogen. When all the SO_2 was, on the other hand, removed by boiling in a stream of nitrogen and the filling occurred in a stream of nitrogen, a little oxidation took place and a light yellow film was deposited on the upper part of the hot wall. The results for transfer of ferrous iron were substantially the same whether this occurred or not, as is shown by the second item of Table I compared with the next two. In the case of the second item there was a slight film. In the next two, and in all further cases (except the last item) in which ferrous chloride was present without ferric, the trace of SO_2 prevented any film formation. In the case of the last item the SO_2 was probably too successfully removed in the apparatus by allowing the uppermost part to come momentarily to boiling under partial vacuum after the steam had been on for an hour, and a thin metallic-looking film was formed along the upper third of the hot wall. The result of this experiment agrees with the others.

When solutions containing ferric chloride and HCl (1*M*) are subjected to diffusion, hydrolysis still takes place on the hot wall, a crust forming on its upper part. Portions of the crust occasionally drop loose and fall to the bottom, where they perhaps redissolve in part in the strong HCl (about 2*M*). The hydrolysis makes, therefore, the interpretation of the results somewhat uncertain, but any enrichment observed at the lower end is presumably too high. Thus when negative enrichments are found they are probably correct as to sign. A 28-hour experiment with a solution 1*M* HCl and 0.5*M* $FeCl_3$ showed -32 percent effect. Three experiments with a solution 1*M* HCl, 0.5*M* $FeCl_2$ and 0.5*M* $FeCl_3$, running for 43, 24, and 39 hours, showed percent effects for $FeCl_3$ $+26$, $+7$ and -3.6, respectively, with corresponding percent effects for $FeCl_2$ -34, -17 and -12. These experiments confirm that ferric chloride can show a negative effect in mixtures and that ferrous chloride does so.

We cannot guarantee that the times were long enough for these mixtures of four components. It may be that more than one steady state of approximately the same stability is possible for such complicated mixtures.

Discussion

To account for the fact that in binary gaseous solutions the heavier species is always found to be enriched at the cold (and low) end of the gradient a simple approximate theory has been offered.[3] The theory of Chapman[4] also accounts for this and allows of small modification of result for molecules of widely different diameters.

Table II. *Transfer of sodium acetate in mixtures with acetic acid in apparatus No. 1.*†

Moles acetate per liter	1.5	1.5	1.5	1.5	1.2	1.2	0.55
Moles acid per liter	0.17	0.17	1.0	1.0	0.14	0.14	0.063
Hours	20	22	23	24	25	25	<72
Concentration ratio	1.88	2.17	2.05	2.05	2.23	2.15	2.64
Percent effect	54	66	66	66	68	64	90

† In the last experiment repairs were needed on the apparatus and 72 hours is the total time, greater than the effective time.

So far, it appears to be a fact that also in binary liquid mixtures the heavier component is enriched at the cold end, even though the heavier component has the smaller molecular weight, as in acetone-water solutions.[5]

[3] L. J. Gillespie, J. Chem. Phys. **7**, 530 (1939).
[4] Sydney Chapman, Phil. Trans. (London) **A217**, 115 (1917).
[5] K. Clusius and G. Dickel, Naturwiss. **27**, 148 (1939).

TABLE III. *Densities of some solutions. M = moles per liter of solution.*

SOLUTION	DENSITY AT 25°
0.5M in HCl and $\frac{1}{6}M$ in $FeCl_3$	1.0312
$\frac{1}{6}M$ in $FeCl_3$	1.0210
0.5M in HCl (made up at 25°)	1.0060
0.5M in HCl (made up at 18°)	1.0076

In the statement of this fact we may understand the heavier component of a binary mixture to be that one which has the greater density when pure, or, and perhaps somewhat better—we may define the heavier component to be that one which increased the density of the solution when it is added at constant temperature and pressure; i.e., that one of a binary mixture for which the function

$$f_i = m_i(\partial\rho/\partial m_i)_{T,\,p,\,m\neq i} = a_i(1-a_i)(\partial\rho/\partial a_i)_{T,\,p,\,a/(1-a_i)\neq i} \quad (1)$$

is positive, where ρ is the density of the solution, m_i is the mass of the substance i and a_i is the mass of the substance i divided by the total mass.

The function is of course positive for that component of a binary ideal gas mixture which has the greater molecular weight.

The same definition recommends itself for the consideration of solutions containing more than two components. For any solution the sum of the functions for all the components is zero by Euler's theorem for homogeneous functions of the zero order, and hence at least one component must be heavy, and at least one must be light (except for the trivial case at a point where the density at constant T and p is a maximum or a minimum).

The rule holds for all the experiments that have come to our attention, including our own on binary mixtures, that the cold-end enrichment in a binary liquid or gaseous solution has the same sign as the function f.

But from the results here reported for the chlorides of iron in HCl solution it appears that this rule does not always apply to ternary mixtures.

In the case of ferric chloride some density data of Kanitz[6] together with the data for HCl from the *International Critical Tables* indicate that the function f_i for ferric chloride is positive as usual (though the cold-end enrichment was found to be negative). His densities are relative to water at 25° and have been computed relatively to water at 4° for Table III.

[6] A. Kanitz, Zeits. f. physik. Chemie **22**, 336 (1897).

Rotational Isomerism in the Alkyl Halides

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RECENTLY Cleveland and Murray[1] have made tentative assignments of the observed Raman shifts in $C_{12}H_{25}Br$ on the basis of the co-existence of two rotational isomers differing by the rotation of the CH_2Br group through 180°. This is in accordance with the ideas of Kohlrausch and his co-workers.[2] Sufficient data[2–7] have been accumulated to re-examine this question. That rotational isomerism does exist is evident from many considerations, but that the forms present in the alkyl halides are the *trans*- and *cis*-configurations is open to question.

The characteristic C—Br vibration in CH_3Br is 603 cm^{-1}.[3] This drops to 566 cm^{-1} in C_2H_5Br. Rotational isomerism gives rise to two C—Br frequencies, 563 and 648 cm^{-1}, in C_3H_7Br. The corresponding values are 563,642 and 564,642 cm^{-1} in C_4H_9Br and $C_5H_{11}Br$, respectively. These values remain practically constant as one proceeds to higher members of this series. For instance the values reported for $C_{12}H_{25}Br$ [1] are 563 and 647 cm^{-1}. The same phenomenon is observed for the corresponding chlorine and iodine compounds.[3] Thus it can be said that these vibrations are only dependent upon the substituent directly attached to the C atom adjacent to the CH_2X group. Hence we are essentially dealing with a molecule of the type CH_2XCH_2Y as far as these vibrations of the CH_2X group are concerned—all CH_2 or CH_3 groups in Y beyond the first being too far removed to influence them. Therefore one would expect these molecules to be similar to the 1–2 dihaloethanes as far as the CH_2XCH_2Y group is concerned. That this is so is clearly indicated when we consider that the C—Br vibrations in CH_2BrCH_2Br are 551 and 659 cm^{-1}. In CH_2BrCH_2Cl they are 568 and 662 cm^{-1} although the assignment is not so certain in this case. These considerations indicate that *the* CH_2X *group has the same orientations* with respect to the CH_2Y group as in the 1–2 dihaloethanes.

The present accepted interpretation is that the dihaloethanes exist in two forms, the halogens *trans* and *cis* to each other. Mizushima and Morino[4] have quite definitely shown, by means of the Raman effect, that the *trans*-form of CH_2ClCH_2Cl and CH_2BrCH_2Br is the only isomer present in the solid state. Since these same Raman lines are present in the liquid, one of the two forms must be the *trans*-form. But is the *cis*-configuration the other form? The great difficulty in a *cis*-form is to account for its stability. Kohlrausch and his co-workers[2] have recognized this fact but maintain that the *cis*-form is the only other form (besides the *trans*) which possesses symmetry. This requirement is necessary in order to account for the large number of observed depolarized lines. However, they have overlooked the C_2 forms. This is the configuration (in ethylene halides) which results when the CH_2X groups are rotated 120° from the *trans*-position. The *trans*-, *cis*-, and C_2 con-

[1] F. F. Cleveland and M. J. Murray, J. Chem. Phys. **8**, 867 (1940).

[2] K. W. F. Kohlrausch and co-workers, (*a*) Zeits. f. physik. Chemie **B18**, 61 (1932); (*b*) *ibid.*, **B26**, 209 (1934); (*c*) *ibid.*, **B29**, 274, 292 (1935); (*d*) *ibid.*, **B32**, 407 (1936); (*e*) Monats. f. Chemie **65**, 185 (1935); (*f*) Ber. **73**, 159 (1940).

[3] The data for the C—X vibrations are from W. D. Harkins and R. R. Haun, J. Am. Chem. Soc. **54**, 3920 (1932) Table IV. The data for CH_2BrCH_2Br and CH_2BrCH_2Cl are from Ta-You Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (China Science Corp., Shanghai, 1939).

[4] (*a*) Mizushima, Morino and Higasi, Sci. Pap. Inst. Phys. Chem. Research (Tokyo) **25**, 159 (1934); (*b*) Mizushima, Morino and Kozima, Sci. Pap. Inst. Phys. Chem. Research (Tokyo) **29**, 111 (1936); (*c*) Kozima and Mizushima, Sci. Pap. Inst. Phys. Chem. Research (Tokyo) **31**, 296 (1937).

[5] (*a*) Wierl, Phys. Zeits. **31**, 366 (1930); Ann. der Physik **13**, 453 (1932); (*b*) Beach and co-workers, J. Chem. Phys. **6**, 639 (1938); J. Am. Chem. Soc. **61**, 303, 3127 (1939); (*c*) Smythe, Dornte and Wilson, J. Am. Chem. Soc. **54**, 3191 (1932); (d) Lennard-Jones and Pike, Trans. Faraday Soc. **30**, 830 (1934); (*e*) Altar, J. Chem. Phys. **3**, 460 (1935); (*f*) Beach and Stevenson, J. Chem. Phys. **6**, 635 (1938); (*g*) Zahn, Phys. Rev. **38**, 521 (1931); *ibid.*, **40**, 29 (1932); (*h*) Smythe and McAlpine, J. Am. Chem. Soc. **57**, 979 (1935); (*i*) Lennard-Jones, Proc. Phys. Soc. **43**, 475 (1931).

[6] (*a*) L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, second edition, 1940); (*b*) Conn, Kistiakowsky and Smith, J. Am. Chem. Soc. **61**, 1868 (1939).

[7] C. Sage, "Studies in molecular structure" (Ph.D. thesis), University of Minnesota (1940).

FIG. 1. Possible rotational isomers of CH_2XCH_2X. Primed letters refer to atoms on one C atom while unprimed letters refer to atoms on the other C atom. The view is along the C−C axis.

figurations are represented in Fig. 1. The assumption that the two isomers present in the liquid state are the "staggered" (*trans*- and C_2) forms correlates much better with the observed data. In Table I is given the number of depolarized lines under 1600 cm^{-1} expected from the various possible forms in the ethylene halides. The *trans*-form gives 2, the *cis* 9 and the C_2 configuration 6. Actually eight are observed.[2f] Thus it would seem that the *trans*- and the C_2 forms are the two isomers present in the liquid state. This interpretation is in harmony with the other data. For instance, the number of observed depolarized lines in the Raman spectrum of CH_2ClCH_2Br are better accounted for if we assume "staggered" forms only; the explanation of electron diffraction patterns and dipole moment measurements on dihaloethanes[4a, 5] requires potential curves which have two minima 120° ("staggered") from the *trans*-configuration. It is interesting to point out[7] in this regard that Wierl's[5a] data from electron diffraction measurements on 1,2 dichloroethane show the existence of two Cl−Cl distances, 4.4±0.1 and 3.2±0.1A (which he interpreted as being due to the presence of the *trans*- and *cis*-forms, respectively). In terms of known interatomic distances and bond angles:

$$d^2_{Cl-Cl} = 7.65 + 5.85(1 - \cos\theta)$$

where $\theta = 0$ for the *cis*-form. This gives 4.4A for the *trans*- and 2.77A for the *cis*-form. If 3.2A is due to the *cis*-isomer the molecule must be under tremendous strain. Yet if one assumes that the second form is the "staggered," C_2 configuration and sets $\theta = 60°$, the Cl−Cl distance is 3.1A in good agreement with the observed value.

TABLE I. *Depolarized Raman lines under 1600 cm^{-1} from different configurations of* CH_2XCH_2X.*

	EXPECTED	OBSERVED
From *trans*	2	
From *cis*	9	8
From C_2	6	

* From Kahovec and Kohlrausch[2f] and C. Sage.[7]

For no molecule of this type has an "eclipsed" isomer been proved to exist. Even for ethane the evidence appears better for the "staggered," D_{3d} form.[6] Thus it can be said that the dihaloethanes in the liquid state most probably possess only staggered forms. This leads to a *trans*- and a C_2 configuration in the case of the ethylene halides. Moreover alkyl halides of the type CH_2XCH_2R act like dihaloethanes as far as the vibrations of the CH_2X group are concerned, and hence the CH_2X group should have the same rotational configurations with respect to the CH_2R group, i.e., a *trans*-form and one in which the CH_2X group is rotated 120° from the *trans*-configuration.

Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Note on the Chain Photolysis of Acetaldehyde in Intermittent Light

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February 4, 1941

IN a note referring to the use of intermittent light in investigating the photolysis of acetaldehyde Messrs. Haden, Meibohm and Rice[1] deduce an upper value of 16.0 kcal. for the activation of the reaction

$$CH_3+CH_3CHO=CH_4+CH_3CO.$$

In this connection it is of interest to compare the value of 9.8 kcal. obtained by the present writer with Dr. Akeroyd[2] for the same reaction at about the same temperature (200–350°C) from a measurement of the temperature coefficient of the photolysis of acetaldehyde. This figure is not an upper value, and when compared with the figure of Haden, Meibohm and Rice indicates that a factor of about 6×10^{-3} should be introduced to allow for the necessity of orientation in the colliding molecules.

A comparable figure of 16.0 kcal. was deduced for the reaction

$$H+HCHO=H_2+HCO.$$

[1] Haden, Meibohm and Rice, J. Chem. Phys. **8**, 998 (1940).
[2] E. I. Akeroyd and R. G. W. Norrish, J. Chem. Soc. 890 (1936).

The Photovoltaic Effect

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February 20, 1941

UNDER the above headline Colin G. Fink and Edward Adler[1] have recently published a theory of the Becquerel effect supposedly based upon the theory of absolute reaction rates whose characteristic coefficient, however, is absorbed by separately introduced factors. The apparently new in the treatment boils down to introducing into the well-known equation[2] for the cathodic overvoltage as a function of current density a term accounting for the transition of photo-electrons from the electrode to the electrolyte: $i_p=kI$, where i_p is the photocurrent; I, the light intensity; k, a constant depending on the nature of the cell and the wave-lengths applied. Hence a relation between light intensity and potential is derived for open circuits. The formula obtained is in agreement with the experimental light intensity/potential curve in the range of small and medium intensities. In the range of greater light intensities, however, the empirical curve tends to a "saturation potential," as should be expected, while the theory of the authors leads to ever-increasing potentials with increasing light intensities.

The authors are well aware of this discrepancy and suggest that it might be due to a limitation in the number of photo-active centers. It is hard to visualize how this assumption could help to a better understanding. Nevertheless, the otherwise sound foundations of the theory can be maintained if the simple quantum rules governing the transition of electrons are properly taken into account, i.e., "the transfer of electrons is impossible if there are no vacant energy levels to which the electrons can be transferred."[3] Of course, there are energy levels of excited states, but they certainly lie much higher than 1 electron volt. In easy reach, on the other hand, are the unoccupied levels of the adsorbed positive ions which, anyhow, serve as acceptors for the "dark" electrons.

Accordingly, the term kI of Fink and Adler has to be substituted by $\overset{+}{a}_{ads}k'I$, where $\overset{+}{a}_{ads}$ is the activity of the adsorbed positive ions as obtaining under the influence of light. It can easily be seen that with this correction the theory covers the whole range of the empirical curve.

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Crystal Density of Native Cellulose

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A WIDE range is covered by the values employed for the density of cellulose, designated variously as "compressed bulk," "natural," "apparent," "assumed," etc. The divergence in density values is ascribable to the different degrees of porosity in the test samples. In recent years values in the neighborhood of 1.50 g/cc have been generally used, where the cellulosic mass is assumed to be continuous (nonporous), with some degree of order among the cellulose chain molecules. In 1937, however, a mean value of 1.585 g/cc for the density of alpha-cellulose in standard cotton linters was obtained by Stamm and Hansen[1] by a method in which the void spaces were filled with helium. Of the 21 values reported by them, 1.585 g/cc is believed to be the most reliable as the true density of cellulose, because of the method used and of the fact that it is for the most highly purified cellulosic material. Aside from the soundness of the underlying theory, this density value is unique in that it is distinctly higher than any previously reported, and is the only one in agreement with

the density calculated from the modern (Meyer's revised) model[2] of the unit cell of native cellulose.

Using Meyer's dimensions for the unit cell and a molecular weight of 324.16 for the cellobiose residue ($C_{12}H_{20}O_{10}$) a theoretical density of 1.582 g/cc has been calculated by this writer. In the construction of the unit-cell model on which these calculations are based, an *approximate* density is required to supplement the x-ray diffraction data, as a contribution to the general plan according to which the x-ray data are to be interpreted. However, the dimensions which are ultimately assigned to the unit crystal, and the density deduced therefrom, are clearly not functions of a prior density. The x-ray data are the same for celluloses of different origins.

While frequent need arises for the "true" or "crystal" density of cellulose in investigations on cellulosic materials and fibers, no notice appears to have been taken in the literature of the excellent agreement between Stamm and Hansen's value and the theoretical value. Because of this agreement, Stamm and Hansen's results appear as an experimental verification of the Meyer model. On the other hand, the unusually high value reported by Stamm and Hansen finds justification in the theoretical model. The most persistent, systematic, experimental error to be expected in density measurements on cellulose is that arising from void spaces. The low values previously reported differ from the theoretical value in the direction which would be expected if inadequate correction is made for porosity. All of these considerations greatly enhance the reliability of 1.582–1.585 g/cc as the density of native cellulose in the continuous crystal lattice.

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One-Sided Polarization of Ions in Vapor Molecules

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THE tightening of anions and loosening of cations was demonstrated recently[1] in an especially simple way by the deviations from additivity of lattice distances and volumes of ionic crystalline substances of high symmetry. The occurrence of these volume effects also in the case of a one-sided interaction of ions has been shown indirectly by considering the individual behavior of the apparent volume of dissolved strong electrolytes.[1] A direct proof for the one-sided effects can be found in the gradation of interionic distances in the vapor molecules of alkali[2] and thallous[3] chlorides, bromides and iodides, measured by the electron diffraction method. According to the authors, the values have an accuracy of between ±0.01 and ±0.04A, so that only considerable deviation from additivity can be interpreted with certainty as due to these polarization effects.

In vaporized sodium and potassium halides, the diminution of the size of the anion can be expected to be stronger

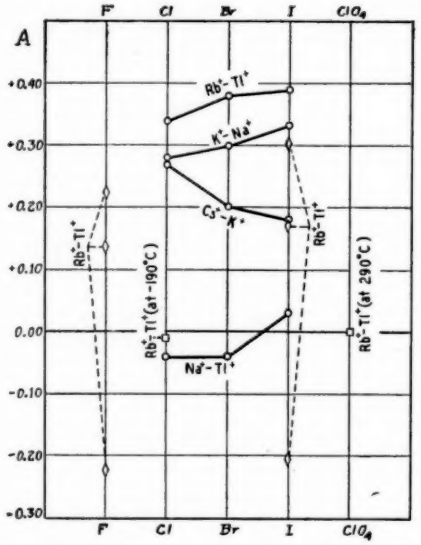

FIG. 1. Comparison of interionic distances in vapor molecules (○) cubic crystals (□) and in rhombic TlF and TlI with cubic RbF and RbI (◇).

than the increase of the size of the cation. Since the polarizability increases from Cl^- to I^- and the polarizing field of Na^+ is stronger than that of K^+ one understands that the difference in the interionic distances between K^+ and Na^+ increases from Cl^- (0.28A) to I^- (0.33, see Fig. 1). On the other hand the difference between Cs^+ and K^+ decreases from Cl^- (0.27) to I^- (0.18) which indicates that at least in the vapor molecules of the CsCl the loosening of Cs^+ by Cl^- is stronger than the opposite effect.

In their high temperature cubic form $TlClO_4$ and $RbClO_4$ have[4] a unit cell of identical edge length (7.7$_0$A), which confirms V. M. Goldschmidt's conclusion that in crystals in which the polarizing effects are weak, Tl^+ and Rb^+ are of equal size. The outer electronic system of Tl^+ consists of an 18-electron shell with two extra electrons. Cations without a rare gas structure exhibit, in general, stronger polarizing effects on anions than those of rare gas type. On the other hand, the polarizability of Tl^+ (R_∞=9.5 cc) is larger even than that of Cs^+ (6.5 cc). Thus, the interionic distances of TlCl (3.24$_9$) and RbCl (3.24$_1$) at −190°C, where both have the CsCl structure,[5] show that here the stronger tightening effect of Tl^+ on Cl^- is just balanced by the stronger loosening of Tl^+.

However, as a result of the one-sided action within the vaporized molecules, the interionic distance in TlCl (2.55) is much smaller than in RbCl (2.89) and only a little larger than in NaCl (2.51); in TlI the distance (2.87) is even smaller than in NaI (2.90).

The short distances within the thallous halide molecules show a strong deformation of ions and confirm the conclusion,[6] based on absorption spectra, that their structure is nearer to covalent than to ionic. This explains the fact that TlCl is distinctly less dissociated[7] in aqueous solution than alkali halides, as well as its low boiling point (806°C; that of RbCl is 1383°).

In connection with these one-sided polarization effects, it is of interest that in both the rhombic TlF and TlI, there different interionic distances occur. In TlF each ion is connected with three pairs of oppositely charged ions at the distances 2.59, 2.75 and 3.04A.[8] In TlI there is one neighbor at the distance 3.36, four are at 3.49 and two at 3.87A.[9]

The smallest of the three distances lies between those of the corresponding solid Na- and K-salts. The largest is nearest to that in CsF (3.00) and CsI (3.95), respectively. One can assume that the longest distance in both TlF and TlI is due to the loosening effect by the anions interpenetrating the Tl^+ and is influenced especially by the two extra electrons in the outer shell of Tl^+, which contribute to its high polarizability. The smallest distance must be due to the tightening of the anions by Tl^+.

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Thermal Transitions in Ammonium and Silver Trihydrogen Paraperiodates*

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At low temperatures the salts KH_2PO_4 and KH_2AsO_4 become spontaneously polarized; an entropy change[1] and corresponding thermal effect are associated with the transition from the polarized to the unpolarized state. According to the theory of the transition as given by Slater,[2] the unusual properties of these salts are due to the various arrangements of the hydrogen ions which form hydrogen bonds joining the phosphate or arsenate groups to each other. Insofar as the hydrogen bonds are concerned, the structure[3] of $(NH_4)_2H_3IO_6$ is similar to that of KH_2PO_4 except that the octahedral IO_6 ion is linked to neighboring paraperiodate groups by six hydrogen bonds while the tetrahedral phosphate group has only four hydrogen bonds. In both cases the hydrogen bonds are unsymmetrically arranged around the central group and a preferred orientation of the hydrogens at low temperatures is possible. This configuration of lowest energy is the polarized form of KH_2PO_4.

In view of these similarities, one would expect a transition in $(NH_4)_2H_3IO_6$ similar to the transition in KH_2PO_4 but with a somewhat higher entropy change due to the larger number of hydrogen bonds.

Preliminary measurements were made in a simple cooling-curve apparatus and a maximum was found in the heat capacity of the ammonium trihydrogen paraperiodate at 254°K. This transition is presumably caused by the hydrogen bonds, although there is a possibility that the ammonium groups, which cause similar transitions in many ammonium salts, are responsible. $Ag_2H_3IO_6$, which is isomorphous with the ammonium salt, has a transition with a maximum in the heat capacity at about 227°K. The reorientation of the hydrogen bonds is the only plausible explanation for this transition, and the presence of the transition is additional evidence that the formula for this salt is not $Ag_4I_2O_9 \cdot 3H_2O$ as it is frequently written. The corresponding sodium salt, $Na_2H_3IO_6$, has a different external crystallographic symmetry and exhibits no transition between liquid air and room temperature.

The silver and ammonium salts would have zero entropy at the absolute zero, because an ordered arrangement of the hydrogen bonds occurs below the transition temperatures. Without further information concerning the positions of the hydrogens in the sodium salt, it is impossible to say whether or not an entropy calculation from low temperature heat capacity data would be correct. A residual entropy associated with a random orientation of the hydrogen bonds may persist to the lowest attainable temperature, as in the case of ice,[4] or an ordered arrangement of zero entropy may already exist at room temperature.

The presence of the transitions in the ammonium and silver salts leaves little doubt that the hydrogen bonds are responsible. On the basis of the hydrogen bond theory, the total entropy change associated with the transitions in the trihydrogen paraperiodates is $R \log 5/2$ in contrast to $R \log 3/2$ for the dihydrogen phosphates. Further studies are planned to test this prediction, and to investigate the spontaneous polarization and anomalous piezoelectric effect which are also predicted.

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Erratum: The Temperature Coefficient of the Conductance of Potassium Chloride in H_2O-D_2O Mixtures

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In this article, Figs. 1 and 2 were interchanged. Figure 1 should be Fig. 2. with the legend denoted as Fig. 2. Figure 2 should be Fig. 1 with the legend denoted as Fig. 1.